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Research on Graphite Reinforced Glass Matrix Composites

J.F. Bacon, K.M. Prewo

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June 1977

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Langley Research Center
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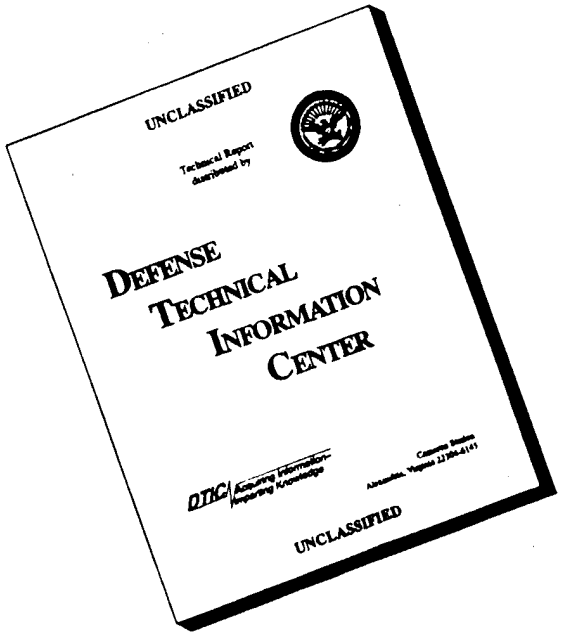

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Research on Graphite Reinforced Glass Matrix Composites

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ABSTRACT

This report contains the results obtained in the first twelve months of research under NASA Langley Contract NAS1-14346 for the origination of graphite-fiber reinforced glass matrix composites. Included in the report is a summary of the research by other investigators in this area. The method selected to form the composites consisted of pulling the graphite fiber through a slurry containing powdered glass, winding up the graphite fiber and the glass it picks up on a drum, drying, cutting into segments, loading the tape segment into a graphite die, and hot pressing. During the course of the work, composites were made with a variety of graphite fibers in a C.G.W. 7740 (Pyrex) glass matrix. The graphite fibers used included Hercules HMS, Hercules HTS, Thornel 300S, and Celanese DG-102 and, of these, the Hercules HMS and Celanese DG-102 graphite fibers in C.G.W. 7740 gave the most interesting but widely different results.

Hercules HMS fiber in C.G.W. 7740 glass (Pyrex) showed an average four-point flexural strength of 848 MPa or 127,300 psi. As the test temperature was raised from room temperature to 560°C in argon or vacuum, the strength was higher by 50%. However, in air similar tests at 560°C gave a severe loss in strength. These composites also have good thermal cycle properties in argon or vacuum, greatly increased toughness compared to glass, and no loss in strength in a 100 cycle fatigue test.

Celanese DG-102 fiber in C.G.W. 7740 glass (Pyrex) had a much lower flexural strength but did not suffer any loss in this strength when samples were heated to 560°C in air for 4 hrs.

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Research Services on Graphite Reinforced Glass Matrix Composites

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I. SUMMARY

Fiber reinforced composites are widely accepted as structural materials because of their desirable attributes of high strength, high modulus and low density. However, even the best of the organic matrix composites reinforced by carbon, boron or glass fiber is limited in use to temperatures below 300°C. Substitution of a metallic matrix for the organic matrix, such as composites of boron or graphite fiber reinforced aluminum, extends the use temperature range only slightly. By contrast, the graphite fiber reinforced borosilicate glass matrix composite which is the subject of this report has exhibited excellent mechanical properties up to 650°C.

Of the two types of graphite fiber reinforced borosilicate-glass composites whose characteristics are given in detail in this report, the Hercules HMS graphite reinforced composite provides the highest level of structural performance. This system has exhibited a flexural strength of up to 977 MPa (142,000 psi) at room temperature. This high level of strength is maintained up to moderate temperatures becoming greater than 1292 MPa at 600°C, a value equal to the strength of HMS graphite fiber reinforced epoxy specimens tested at room temperature. Above 650°C, bend specimens of the HMS graphite fiber reinforced borosilicate glass do not fracture, but instead deform extensively. Specimens of this composite, when tested for fracture toughness, gave results which compare favorably with aluminum alloys and graphite fiber reinforced epoxy composites. The HMS fiber-reinforced glass composite also displays excellent strength retention after exposure to 100 fatigue or thermal cycles, but it suffers degradation of strength when heated to 560°C in air for 4 hrs. Overcoming this strength degradation will be a major task of the second year's research on these types of composites.

The second type of graphite fiber-borosilicate glass composite discussed in detail is reinforced with Celanese DG-102 graphite fiber. This composite has a flexural strength of 340 MPa (49,600 psi) at room temperature and again it increases in strength by almost 40% as the test temperature is increased to 650°C. The relatively low value of strength for this composite is maintained even after 4 hrs exposure to air at 560°C.

The contract monitor for this program is Dennis Dicus and his helpful comments are greatly appreciated.

II. BACKGROUND

At the inception of this program the sales of high performance fiber reinforced composite materials exceeded a million pounds yearly. In general, most of these composites were organic polymer (epoxy resins, polyimides, polycarbonates, and similar materials) matrices reinforced with a great variety of fibers including Kevlar*, carbon, graphite, fused silica, glass, and boron. In general, almost all of these composites were limited to use temperatures not exceeding 300°C.

At the start of this contract, there were no reinforced glass matrix composites commercially available except the age-old wire reinforced glass used for improving the burglar resistance of homes and stores and the AVCO developed tungsten mesh reinforced fused silica intercontinental ballistic missile nose cones. Yet if one conceives of glass as just a high-temperature thermoplastic, the substitution of a glassy matrix for the low temperature polymers in composite materials seems a natural way to proceed. This concept, however, had attracted sparse attention in the past.

A. Review of the Literature

Siefert (Ref. 1) has patented two glass compositions particularly suitable for producing fiber (stainless steel, boron, graphite) reinforced glass composites by pulling the fibers through a molten glass bath and then through a constricting orifice. He states that the resulting composites exhibit high stiffness, a flexural strength higher than aluminum, high impact resistance (being much more impact resistant than monolithic glass), and a capability to withstand temperatures of 538°C for 100 hrs without loss of properties.

Siefert (Ref. 2) extended his work to boron, tungsten and molybdenum reinforced glass composite formed by fusing the glass coated metal fibers together by drawing the fiber through a glass tube and softening a narrow band of the glass tube around the fiber. His boron fiber glass reinforced matrix had flexural properties of 1103 MPa (160,000 psi), a compressive strength of 2069 MPa (300,000 psi), a modulus of 158 GPa (23 x 10^6 psi) and retained its properties when loaded to 50% ultimate tensile strength and kept in water for 5.7 days as well as after being held at 1000°F for 100 hrs. Finally, samples of his composites when notched and subjected to an impact test were found to have high impact strength and to show no decrease in strength over unnotched samples.

*Registered trademark, DuPont Corp., Wilmington, Delaware

Sambell, et al (Ref. 3) fabricated carbon fiber composites using chopped fibers and magnesia, alumina, soda-lime glass, borosilicate glass, and a lithia aluminosilicate glass-ceramic as matrices. He found that thermal stresses resulting from a mismatch in thermal expansion coefficients ruled out any success with the magnesia, alumina, and soda-lime glass matrices but not with the Pyrex or low expansion glass ceramics. For these he found that the addition of carbon fibers produced substantial increases in the work of fracture and that all composites had lower strengths than the matrix materials if randomly oriented fibers were used (but that the borosilicate glass matrix with partially aligned fibers was stronger and had improved thermal shock characteristics).

Sambell, et al (Ref. 4) continued their investigations using continuous graphite fibers in the same matrix materials, i.e., alumina, magnesia, soda-lime glass, borosilicate glass and a lithia-aluminosilicate glass ceramic. They found that the reinforced glass had a strength sevenfold greater than the unreinforced glass and showed a tenfold increase in work of fracture.

Phillips (Ref. 5) investigated in detail the tenfold increase in work of fracture shown by the 40 vol % carbon fiber reinforced Pyrex glass and attempted to explain the results in terms of the initial rate of release of strain energy during fiber fracture and the interfacial strengths of the fibers during pull out. In Ref. 6, Phillips, et al discussed in detail the mechanical properties of the carbon fiber reinforced Pyrex glass in terms of volume fraction of fiber, the orientation of the fibers, fiber damage during fabrication, matrix porosity, matrix critical strain, interface properties and the mode of failure in bend tests. They found from preliminary stress cycling experiments, at stresses above that at which the matrix cracks are formed, that crack propagation is inhibited by the fibers. They also found that to a first approximation, Young's modulus for the composite is that predicted by the rule of mixtures.

Levitt (Ref. 7) developed graphite fiber reinforced composites where the matrix composition was $Li_2O \cdot Al_2O_3 \cdot nSiO_2$ with n = 3, 4 and 8. He used a drum winding apparatus to produce graphite fiber/ceramic matrix tapes which were then hot pressed to their final dimensions. He obtained fivefold increases in modulus of rupture with no fall off after repeated thermal cycling to 1200°C for all three compositions reinforced by continuous graphite tows. His composites were generally characterized by low porosity, intimate fiber-matrix contact and an uncracked matrix, which was the result of a suitable thermal expansion match between fiber and matrix and the occurrence of a strong fiber-matrix bond. Izod impact energies of 4.2 to 6.3 kJ/m^2 (20 to 30 ft/lb/in.^{2}) for the notched specimens and 15.75 kJ/m^2 (75 ft-lbs/in.^{2}) for the unnotched specimens were obtained at room temperature.

Phillips (Ref. 8) has investigated the interfacial bonding and the toughness of four different carbon fiber reinforced glass and glass-ceramic composites and finds that he can explain his results on the basis of the difference in thermal shrinkage between the glass-ceramic and Pyrex matrices resulting in differences in fiber-matrix interfacial shear bond strength and consequent differences in pull out.

Lange (Ref. 9) found that a significant increase in fracture energy was observed (up to 5 times the fracture energy of the glass without second-phase dispersion) when 40 vol % of 44 micron average size alumina particles were dispersed uniformly in a sodium borosilicate glass and that the flexural strength was almost doubled for the same dispersion.

Hasselman and Fulrath (Ref. 10) developed a fracture theory for a composite system based on a dispersion of alumina particles in a continuous glass matrix and then proceeded to verify it experimentally. They found that for 47.5 vol % of 15 micron (average size) alumina particles, the strength (as determined by four-point bend tests) of the sodium borosilicate glass was increased from 101 MPa (14,700 psi $\pm$ 12.7%) to 162 MPa (23,600 psi $\pm$ 3.7%) in accordance with the predictions of their theory.

B. Background Research on Glass Matrix Composites

Because of the many favorable conclusions stated in the references just cited, UTRC, in the late fall of 1975, turned its attention to research on new high temperature fiber reinforced glass composites. This research was intended to supplant the widely used epoxy resin-glass, boron, or carbon fiber composites which are, as mentioned, limited in service to a few hundred degrees Fahrenheit, by the much higher temperature composites consisting of glass matrices reinforced by graphite, alumina, silicon carbide, or boron nitride fibers. These glass matrix composites should be suitable for use at intermediate to elevated temperatures (700-1100°C) where aluminum composites would fail by melting and nickel matrix composites by lack of thermochemical stability.

This initial research at UTRC was largely in the area of graphite fiber reinforced glass matrices. However, it also included experiments with alumina fiber, silicon carbide fiber, boron fiber, and Borsic (silicon carbide coated boron) fibers. As shown in Table I, even these early experiments gave promising results.

The first five samples in the table were hot pressed at 13.8 MPa (2000 psi) and 15 min dwell time. The best of these data indicated that the addition of carbon fiber even at this early date was capable of giving an approximate tenfold increase in strength compared to the unreinforced glass. In addition,

Table I

Early UTRC Experiments

Mechanical Properties of Hot Pressed Samples
(measured at room temperature except as noted)

Material	Temp. of Hot Pressing (°C)	% Fiber in Sample	3-Point Flexural Strength MPa	(psi)
7740 Glass - Thornel 300	1050	34.4	300	43,500
7740 Glass - Thornel 300	1100	40.5	376	54,500
7740 Glass - Thornel 300	1100		364	52,750
7740 Glass - Thornel 300	1150	40.5	400	58,050
7740 Glass - Thornel 300	1225	40.5	305	44,300
7740 Glass - FP Al_2O_3	1100		138	20,000
1723 Glass - FP Al_2O_3	1100	27	232	33,600
7740 Glass - HM (u)	880		278	40,250
7740 Glass - 5.6B	700	19	383	55,500
7740 Glass - 5.6B	700	30	572	83,000
7740 Glass - 5.6B	700	50	603	87,400
7740 Glass - 5.6B	700	34	532	77,100
7740 Glass - 5.6B	700	34	590	85,600 @ 300°C
7740 Glass - 5.6B	700	34	584	84,700 @ 600°C
7740 Glass - Borsic	700	30	353	51,150
7740 Glass - 8.0B	700	36	587	85,100
7740 Glass - 5.6 SiC	700	36	531	77,000
7913 Glass - Thornel 300	1550	37	186	27,000
7913 Glass - Thornel 300	1600	37	145	21,000
7913 Glass - Thornel 300	1650	37	108	15,700

as the data for the boron fibers in Pyrex glass indicate, these composites can be expected to maintain their structural integrity as well as at least their original flexural strength up to the softening point of the particular glass used as the matrix, in this case, 600°C.

III. MATERIALS USED DURING FIRST YEAR'S EFFORT

A. Graphite Fiber

The types of fibers readily available in this country for a research program on the generation of new types of graphite fiber reinforced glass matrix composites are shown in Table II. It will be noted that they vary widely in several important characteristics such as the number of fibers in each, the strength and modulus of the fiber, the precursor used to make the fiber, and the price. It is perhaps not so obvious that the use of each fiber presents a distinct surface chemistry problem, but if one considers the finish on the fiber surface and the chemical elements found on the fiber surface as shown in Table II the problem is evident. This is particularly true if one examines the distinctive shape of each carbon fiber as shown in Fig. 1. It is apparent, therefore, that any given glass matrix reinforced with a given graphite fiber will show its own characteristic behavior.

To broaden the investigation as much as practicable, UTRC purchased some of each carbon fiber shown in Table III. In examining this table, it is obvious that the so-called low price fibers derived from a pitch base are far from low-priced at this time and possess only a mediocre strength. What is not obvious, however, is that one of the fibers highly considered for this program, namely Thornel 75 WYL 30 1/2, is no longer available. The Celanese DG-102 fiber has proven to be a suitable substitute in modulus although not in strength and the Hercules HMS fiber is a suitable substitute in strength but not in modulus.

B. Glasses

The types of glasses which were considered for use on the UTRC/NASA-Langley program are shown in Table IV. Just as the graphite fibers show individual characteristics, the glasses also vary widely in their nature possessing different coefficients of linear expansion, different chemical compositions, varied environmental stability, and, of course, different temperature working ranges. Although all the glasses in the table have relatively low thermal expansion coefficients, only the titanium silicate glass has an expansion coefficient as low as that of the graphite fibers.

Just how different the working characteristics of these glasses are is shown in Fig. 2. It is apparent, therefore, that any resultant graphite fiber-glass matrix composites will have their own fabrication conditions. The glasses as they actually arrive at UTRC are shown in the scanning electron micrograph of Fig. 3. Although each glass is purchased solely on the basis that ninety percent must pass through a 36.0 mesh screen; actually all glasses contain numerous fine particles under one micron in size, and it is believed that these fine particles contribute greatly to the fabrication process to be described in the next section.

Table II

Carbon Fibers and Their Characteristic Properties

Type of Fiber	No. of Fibers in Tow	Finish Used	Precursor Size of Fiber (microns)	Modulus GPa	Modulus psi x 10^6	Strength MPa	Strength ksi	Density gms/cm^3	Coeff. Linear Expansion cm/cm°C (axial)	Cost per Pound $	Result of Spectroscopic Examination
Hercules HM/PVA	1,000	PVA 0.86	PAN	385	55.9	2427	352	1.850		300	
Hercules HMS	10,000	Oxidized	PAN 7.3	351	50.9	2703	392	1.808	-5.7×10^{-7}	90	High Na, high Si, Cr
Hercules HTS	10,000	Oxidized	PAN 7.6	256	37.2	2830	410	1.658	-3.8×10^{-7}	75	High Na, very high K
Celanese DG-102	384	Oxidized	PAN 8	531	77.0	1724	250	1.96		250	Very low Na highest Fe, Si, Ti, Zr
Thornel 300 Grade WYP30 1/0	3,000	UC 309	PAN 6.9	234	34.0	2482	360	1.76		40	Very high Na, high Cu high Sn, Zn
Thornel 300 Grade WYP90 1/0	1,000	UC 309	PAN 8.4	228	33.0	2655	385	1.75		32	Moderate Na high Mg, Sn, P
Thornel 75 Grade WYL160 1/2	720	PVA	Rayon 6.0	538	78.0	2620	380	1.80		385	Intermediate Na very high P high Ca, Ta, Zn
Thornel 50 Grade WYG130 1/2	720	PVA	Rayon 6.6	393	57.0	2172	315	1.66		320	

FIG. 1

TYPICAL FIBERS AS SEEN IN SCANNING ELECTRON MICROGRAPHS

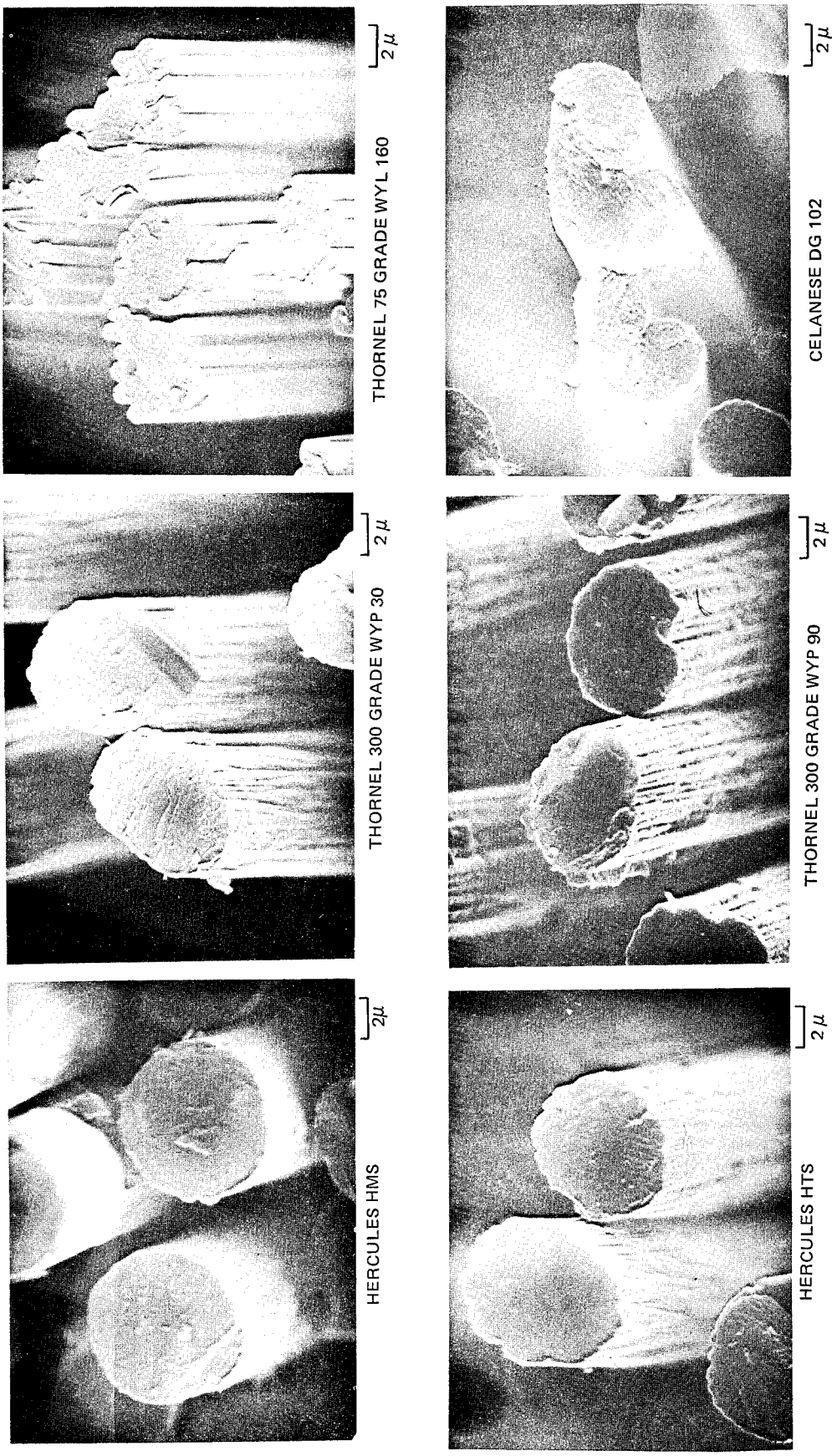

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Table III

Carbon Fiber Obtained for this Study

	Number of Fibers in Tow	Tensile Strength MPa	(ksi)	Young's Modulus GPa	(10^6 psi)	Present Cost ($/lb)
Hercules HTS	10,000	2979	432	234	34	75
Hercules HTS Special	1,000	2875	417	234	34	300
Hercules HM (μ) - PVA	1,000	2427	352	385	55.9	300
Hercules HMS - 10 K	10,000	2344	340	296-331	43-48	90
Hercules HMS - 3 K	3,000	2330	338	370	53.7	175
Thornel 50 WYG 130 1/2	1,540	2172	315	393	57	320
Thornel 75 WYL 160 1/2	1,540	2620	380	538	78	385
Thornel 300 WYP 30 1/2	3,000	2482	360	234	34	40
Thornel 300 WYP 90 1/0	1,000	2655	385	227	33	32
Thornel Pitch VS 0022-1	2,160	1145	166	469	68	55
Thornel Pitch VS 0022-2	2,160	945	137	345	50	55
Thornel Pitch VS 0022-3	2,160	993	144	414	60	55
Thornel Pitch VS 0032-1	720	1282	186	386	56	270
Thornel Pitch VS 0032-2	720	1083	157	400	58	270
Celanese DG 102	384	1724	250	531	77	250

Table IV

Characteristic Properties of Glasses Used

Type of Glass	Nature of Glass	Strain Point $*10^{14.5}$	Anneal Point $*10^{13.0}$	Soften Point $*10^{7.5-8}$	Liquidus	Working Point $*10^{4}$	ρ gms/cm^3	Index of Refract.	Dielectric Constant	Coef. Linear Expansion cm/cm°C x 10^{-7}	Modulus 10^6 psi
C.G.W. 7740	Boro-silicate	510°C	560°C	821°C	1017°C	1252°C	2.23	1.474	4.6	32.5	9.1
C.G.W. 1723	Alumino-silicate	665	710	908	1070	1168	2.64	1.574	6.3	46	12.7
Ferro S	Magnesio-alumino-silicate	760	810	970	1050		2.49	1.547	5.2	29	12.4
C.G.W. 7913	High silica	890	1020	1530	1700		2.18	1.458	3.8	5.5	9.8
C.G.W. 7940	Pure silica	956	1084	1580	1700		2.20	1.459	3.8	3.5	10.5
C.G.W. 7971	Titanium silicate		1000	1500	1600		2.21	1.484	4.0	-2	9.8

*viscosity, in poises

FIG. 2

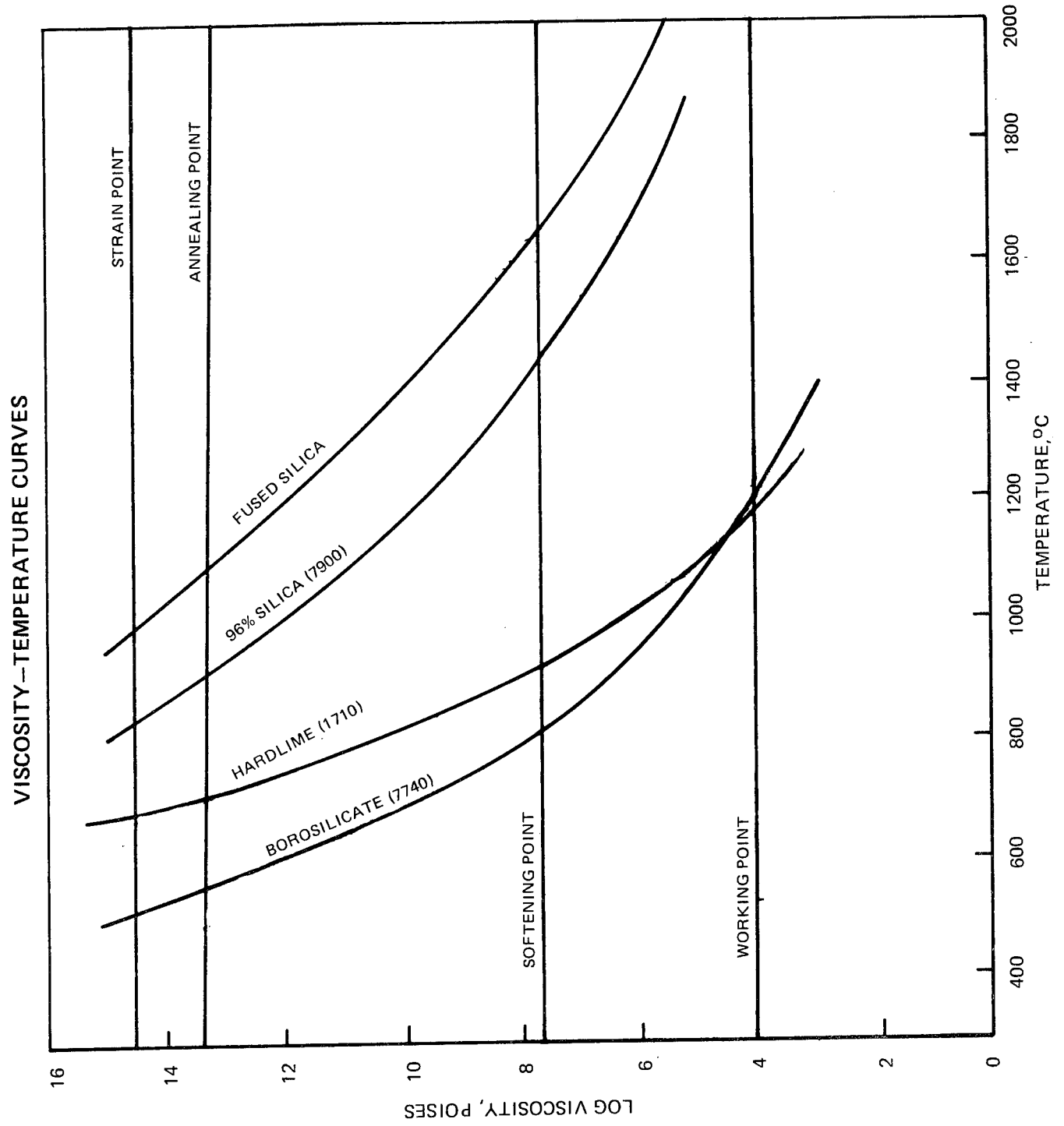

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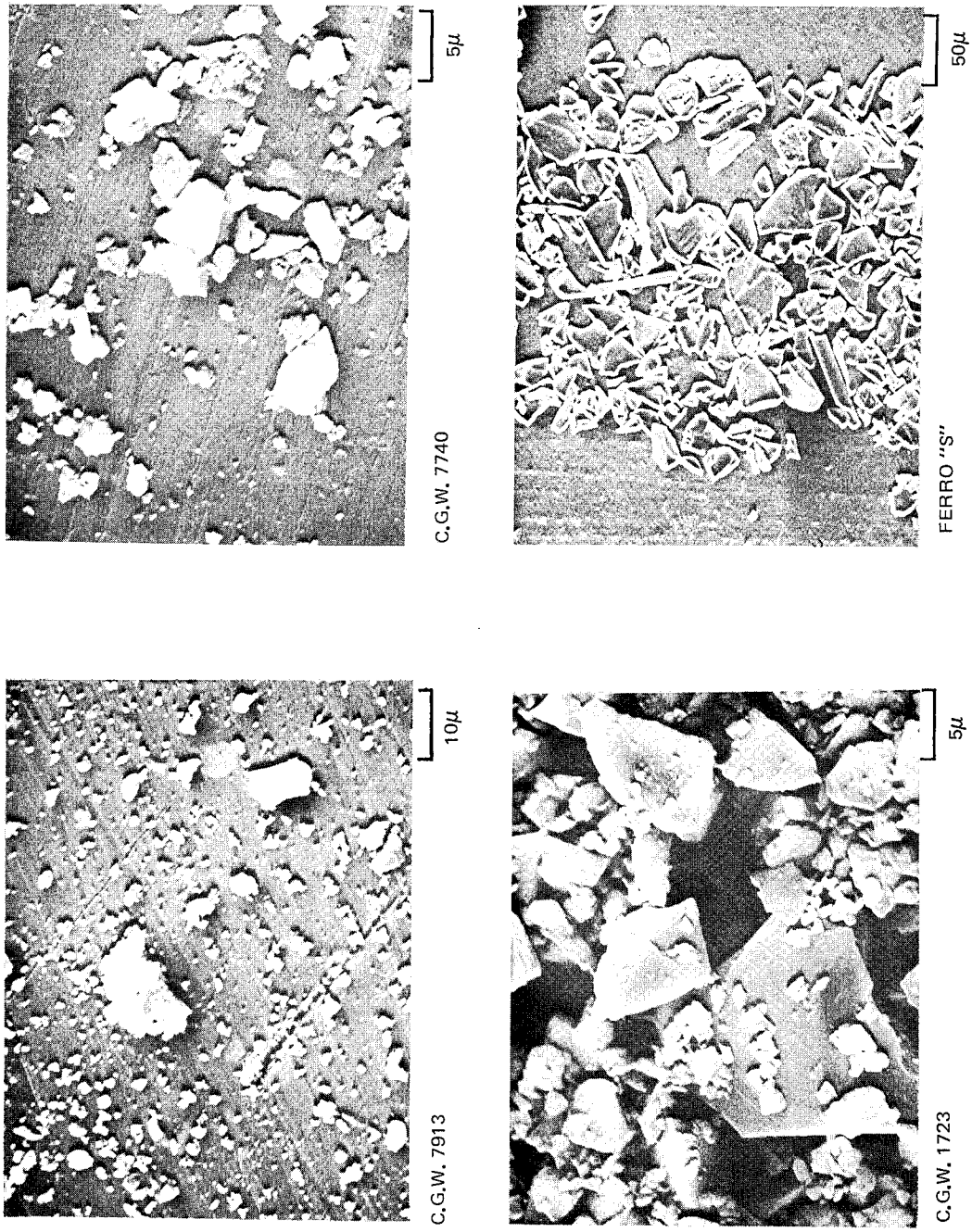
FIG. 3

SCANNING ELECTRON MICROGRAPHS OF GLASS POWDERS



IV. PROCESSING

A. Description of Fabrication Process

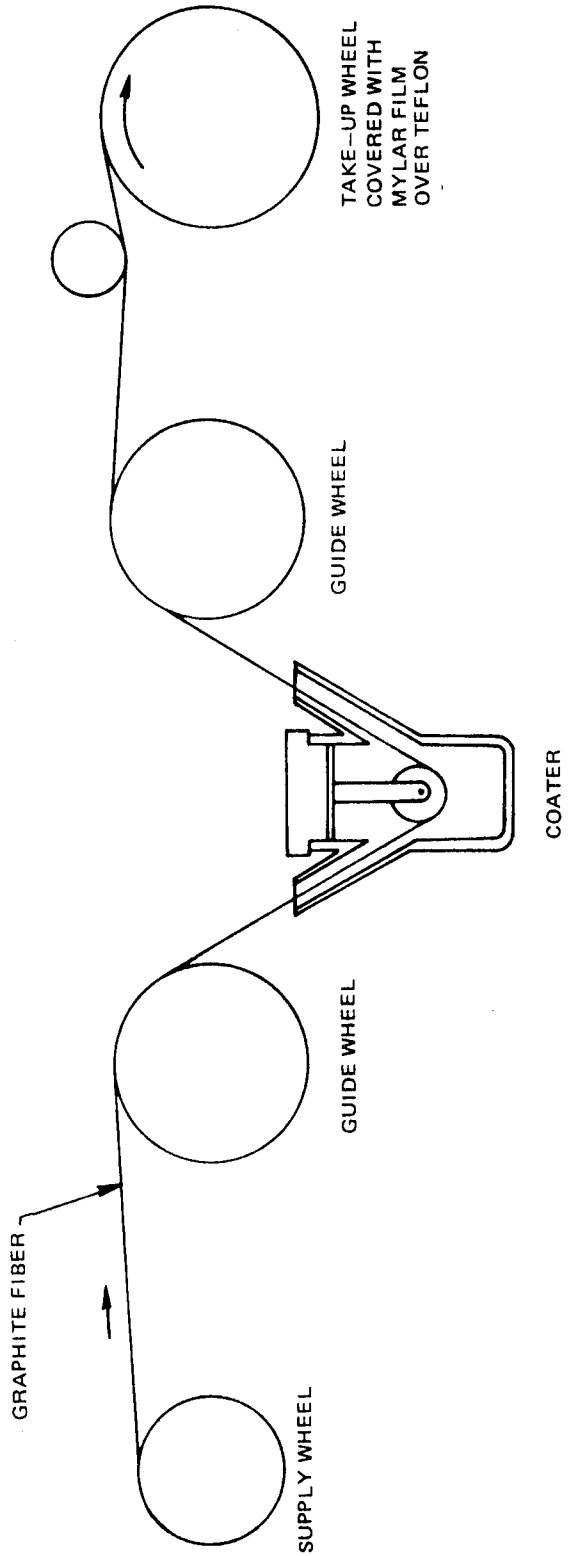
As discussed earlier, several methods exist for coating the fiber as required in the construction of a fiber reinforced glass matrix composite and, indeed, in our earlier evaluation UTRC considered as many as six different processes. However, much the simplest and lowest cost method, if it can be made to work, consists of pulling the graphite fiber tow through a slurry containing the finely ground glass particles.

In the slurry process for coating the graphite fiber with glass, the graphite fiber is unwound from the spool and pulled through an agitated organic solution containing a suspension of fine glass particles. The process is shown schematically in Fig. 4. In greater detail, the continuous graphite tow is unwound from the drum on which it is received at a moderate rate of speed, pulled through a slip comprised of powdered glass, solvent and plasticizer to impregnate the tow, and rewound onto a large rotating drum covered with mylar tape to prevent sticking of the impregnated graphite fiber. The slip may be composed of 40 grams of powdered glass and 3 grams of polyvinyl alcohol dissolved in 100 grams of water to which 2 grams of ethylene glycol is added as a plasticizer. Alternately, the slip may comprise 85 grams of glass in 225 ml of toluene to which 5 grams of polystyrene and 5 drops of tergitol have been added. The large drum is run at one revolution per minute or a linear speed of 5 ft/min. Excess glass and solvent are removed by pressing a squeegee against the drum as it winds. The ground glass used is sized, currently, so that 90% passes through a 325 mesh sieve.

After the tape is dry (sometimes heating with a radiant heat source is necessary to remove excess solvent) it is cut and removed from the drum and then cut into strips or squares which are layed up to give unidirectional or cross-plied fiber alignment and then hot pressed. The hot pressing may be carried out in vacuum using metal dies coated with colloidal boron nitride at pressures of 13.8 to 20.7 MPa (2000 to 3000 psi) and temperatures of 1050 to 1200°C for the common borosilicate glass. Alternately, the hot pressing may be done in argon using graphite dies sprayed with boron nitride powder, pressures of 13.8 to 27.6 MPa (2000 to 4000 psi), and a temperature of 1400°C for the Corning ultra-low expansion glasses. In addition, as each layer of tape is placed in the die, a packet of glass weighing 0.05 to 0.15 grams (the heavier the tape layer, the smaller the glass packet) is inserted between layers in an attempt to achieve a 60 to 70% volume loading of graphite fiber in the composite. The mold is then vibrated to ensure uniform distribution of the glass over the tape surface.

FIG. 4

SLURRY METHOD OF COATING GRAPHITE FIBER



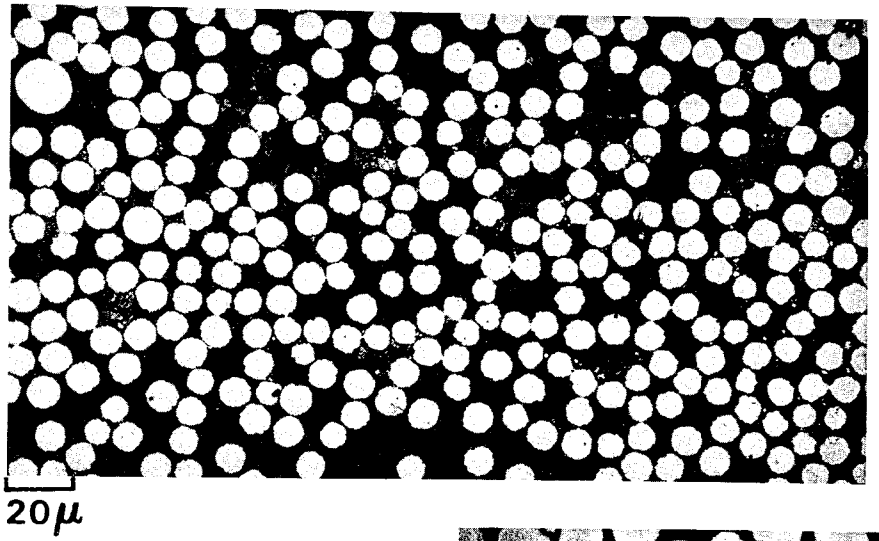
The process just described seems very straightforward. Nevertheless, as is shown in the following section, variables such as hot pressing temperature, hot pressing pressure, hot pressing atmosphere, dwell time in the hot press, amount of glass in the slurry, and amount of glass introduced between layers must all be standardized before an optimum composite can be produced. This learning process can be illustrated by examining Figs. 5, 6 and 7. Figure 5 shows the types of microstructures obtained at a very early stage in the UTRC graphite fiber reinforced glass matrix program as does Fig. 6 but with a second type of graphite fiber. Figure 7, on the other hand, is taken from the third monthly report and shows both the much greater fiber density and uniformity of fiber distribution obtained after 90 days of progress on the program. The fiber density and uniformity of fiber distribution continued to improve, as will be shown by micrographs of the most recent samples in the latter sections of this report.

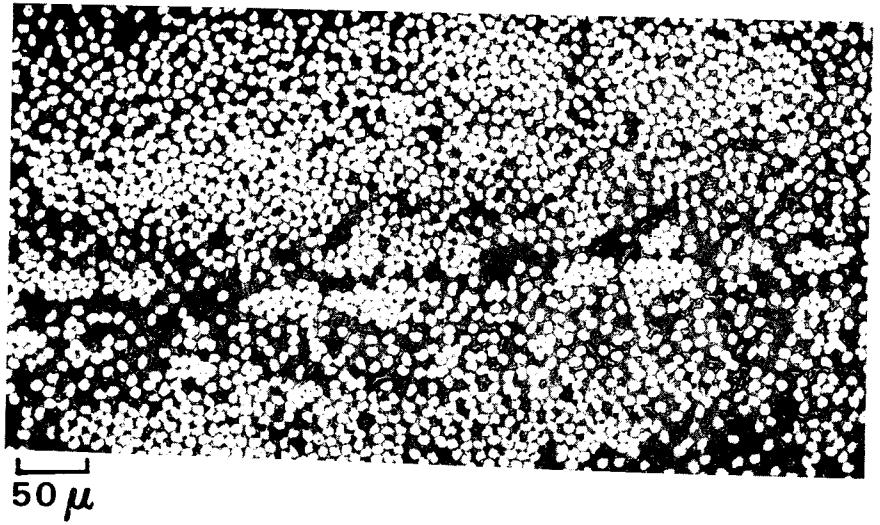
In Table V data are given for all the graphite reinforced glass matrix composites fabricated to date. In this tabulation the temperature and pressure of hot pressing, the type of graphite fiber and the type of glass are the principal variables tabulated against the flexural strengths and densities achieved where these have been measured. The hot pressed sample size is typically 6.35 cm x 2.22 cm x 0.635 cm. From this sample nine flexural samples can be cut and these are typically 5.08 cm x 0.508 cm x 0.127 cm.

B. Effect of Processing Variables and Material Constituents

The procedure for assembling a graphite fiber reinforced glass matrix composite consists of a number of processes each with its own variables. In making the glass coated graphite fiber tape the speed with which the fiber moves through the slurry, the amount of glass in the slurry, the organic constituents in the slurry and their proportions can all be varied. In cutting the tape and stacking it into the die the amount of additional glass introduced between each layer and the number of layers must be determined experimentally. In the actual hot pressing operation the number of temperatures at which we stop to outgas, the hot pressing temperature, pressure, atmosphere and dwell time, the temperature to which the die is cooled before release of pressure, the mechanical fit of the die, and, indeed, even the particular hot press to be used must all be decided. Of course, the types of graphite fiber and of glass used in forming the glass matrix are of great importance. This section will examine the effect five of these variables have on flexural strength.

MICROGRAPHS OF TYPICAL UTRC CARBON FIBER REINFORCED GLASS MATRIX COMPOSITES





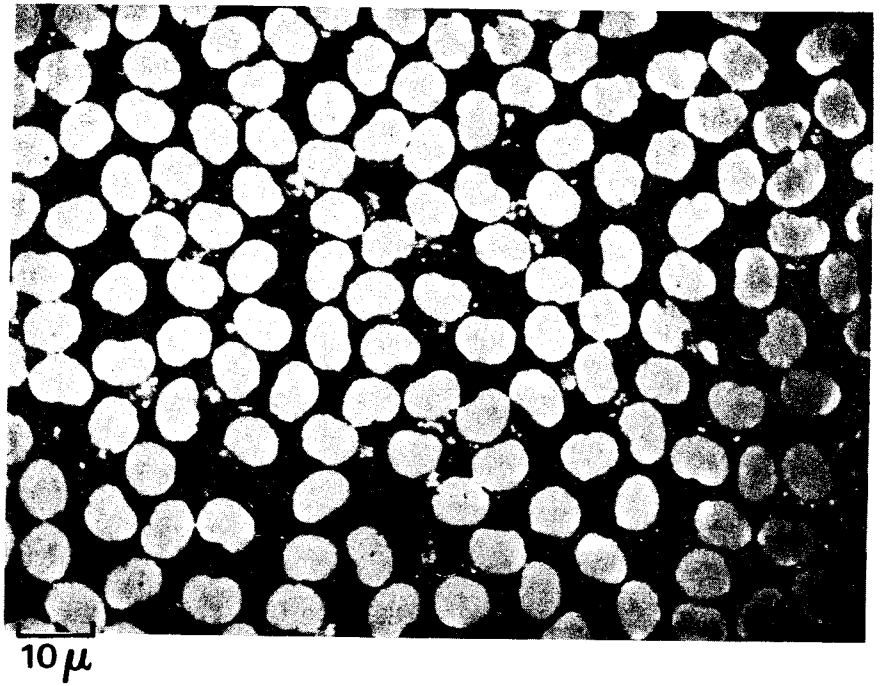


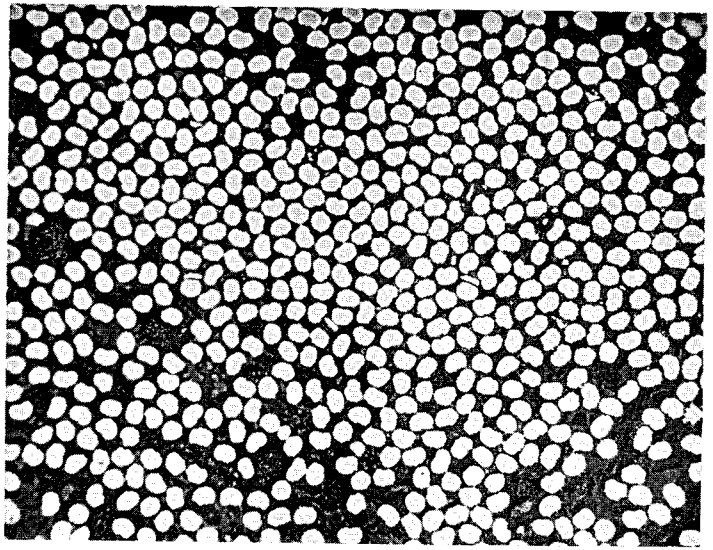
FIG. 5

FIG. 6

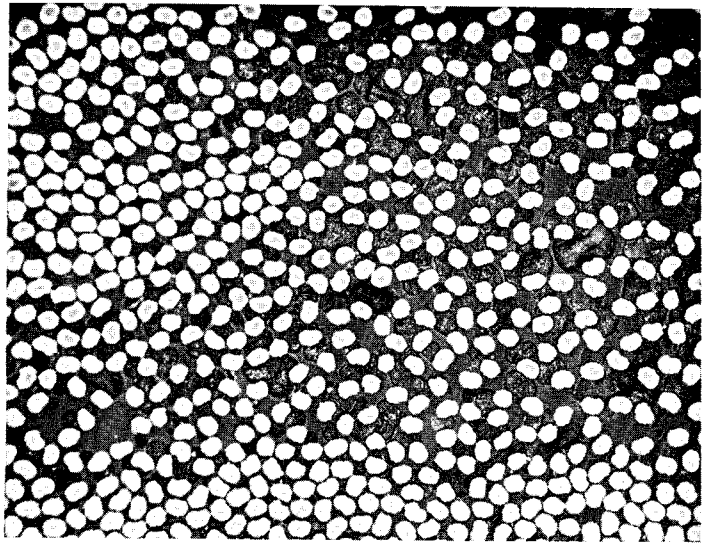
FRACTURE STRENGTH OF THORNEL 75 –GLASS MATRIX COMPOSITE AND MICROGRAPHS OF MATERIAL NEAR THE FRACTURE SURFACE

3 POINT FLEXURAL STRENGTH 359 MPa (52,100 psi)

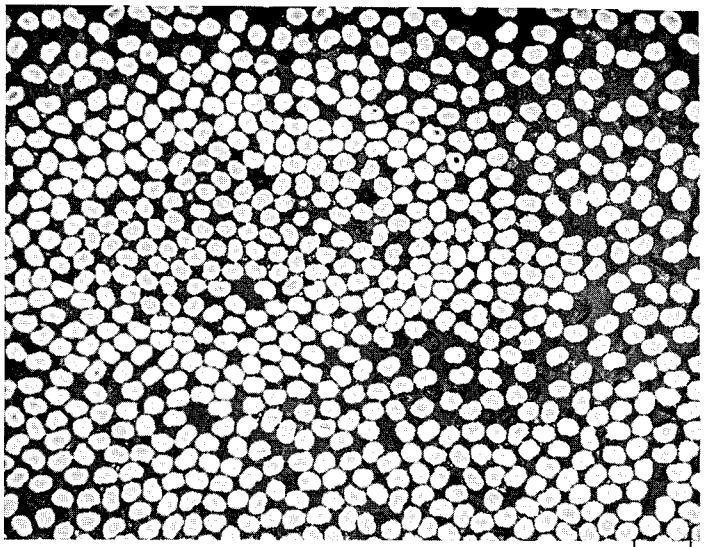
MICROGRAPHS AFTER FRACTURE OF THREE TYPICAL SAMPLES (500X)



LB78–8, 506 MPa (73.4 ksi)



LB80–CR, 638 MPa (92.6 ksi)



LB80–BC, 386 MPa (56.0 ksi)

20μ

FIG. 7

Table V

Graphite Fiber Reinforced Glass Matrix Composites Prepared and Evaluated

Sample	Glass	Fiber	Hot Pressing Conditions Pressure lb/in.^{2}	Temp °C	Three-Point Flexural Strength MPa	psi	Density gms/cm^3	Highest Density Achieved Similar Composite gms/cm^3
Gl 10	7913	Thornel 75	2000	1550	165	24,000	1.585	2.138
LB 11	7913	↓	13.8 MPa	1600	198	28,700	1.695	↓
LB 12	7913		↓	1650	193	28,000	1.605	
LB 13	7913			1550	165	24,000	1.585	
LB 53	7913+7740			1600	319	46,330	2.138	
LB 53B	7913	↓	↓	1600	199	28,900	1.732	↓
LB 90	7740	Celanese DG 102	2000	1120	250	36,300	2.011	2.060
LB 91	↓	↓	13.8 MPa	1120	227	32,800	2.046	↓
LB 92			↓	1115	187	27,100	2.060	
LB 93				1110	330	47,800	2.043	
LB 94				1025	356	57,700	1.936	
LB 95				1050	230	33,400	1.997	
LB 96	↓	↓	↓	1075	289	42,000	1.911	↓
LB 97	7740	Celanese DG 102	2000	1100	342	49,600	1.969	2.060
LB 97B	↓	↓	13.8 MPa	1100			1.980	↓
LB 97C			↓	1100			1.969	
LB 97D				1200			2.025	
LB 97E				1200	*309	*44,800	2.049	
LB 97F				1200			Cracked	
LB 97G				1200			Cracked	
LB 97H				1200			Cracked	
LB 97I	↓	↓	↓	1200			Cracked	↓
LB 98	7740	Celanese DG 102	2000	1120	310	45,000	1.969	2.060
LB 112	8913	↓	13.8 MPa	1850			1.375	
LB 107	7913		↓	1600				
LB 108	7913			1650				
LB 131	7740			1100	227	32,900	1.952	2.060
LB 132	7740	↓	↓	1100	243	35,200	2.000	2.060
LB 135	7740	Hercules HMS	2000	1100	699	100,000	1.960	1.976
LB 135B	↓	↓	13.8 MPa	1120				↓
LB 135C			↓	1100			1.972	
LB 135D				1100	526	76,300		
LB 135E				1100	*574	83,300	1.976	
LB 135F				1200	977	142,000	1.920	
LB 135G				1200	*848	*127,300	1.939	
LB 135H				1200	*577	*83,700	1.957	
LB 135I				1200	*483	*70,100	1.955	
LB 135J				1200			1.949	
LB 135K				1200			1.943	
LB 135L				1200			1.937	
LB 135M				1200			1.955	
LB 135N				1200			1.951	
LB 1350	↓	↓	↓	1200			1.958	↓

*4-Point Flexural Test

Table V (Cont'd)

Sample	Glass	Fiber	Hot Pressing Conditions Pressure lb/in.^{2}	Temp °C	Three-Point Flexural Strength MPA	psi	Density gms/cm^3	Highest Density Achieved Similar Composite gms/cm^3
LB 136	7740	Hercules HMS	2000	1100	648	94,000	1.960	1.976
LB 137	7740	↓	13.8 MPa	1100	648	94,000	1.957	↓
LB 138	7740	↓	↓	1100	661	96,000	1.952	↓
LB 139	7740	↓	↓	1100	↓	↓	↓	↓
LB 140	7740	↓	↓	1100	↓	↓	↓	↓
LB 157	7740	↓	↓	1100	↓	↓	↓	↓
LB 158	7740	↓	↓	1100	↓	↓	1.977	↓
LB 159	7740	↓	↓	1100	↓	↓	↓	↓
LB 171	1723	↓	↓	1120	↓	↓	1.9637	↓
LB 172	1723	↓	↓	1120	353	51,300	↓	↓
LB 173	1723	↓	↓	1120	↓	↓	1.9489	↓
LB 174	1723	↓	↓	1120	↓	↓	↓	↓
LB 147	7740	Hercules HTS	2000	1100	↓	↓	↓	↓
LB 148	↓	↓	13.8 MPa	1100	370	53,700	1.902	1.902
LB 148B	↓	↓	↓	1100	↓	↓	1.597	↓
LB 148C	↓	↓	↓	1100	↓	↓	1.858	↓
LB 148D	↓	↓	↓	1100	↓	↓	1.886	↓
LB 148E	↓	↓	↓	1200	↓	↓	1.865	↓
LB 148F	↓	↓	↓	1200	↓	↓	1.800	↓
LB 149	↓	↓	↓	1100	324	47,000	↓	↓
LB 150	↓	↓	↓	1100	↓	↓	↓	↓
LB 151	↓	↓	↓	1100	↓	↓	↓	↓
LB 152	↓	↓	↓	1100	↓	↓	↓	↓
C2639-2,3	7740	Thornel 300	2000	1100	364	52,750		2.013
C265B-1,2	↓	↓	13.8 MPa	1100	376	54,450	1.931	↓
Gl 1-1,2	↓	↓	↓	1225	304	44,000	1.603	↓
Gl 2a,b	↓	↓	↓	1600	147	21,300	1.955	↓
Gl 3a,b	↓	↓	↓	1650	109	15,800	2.013	↓
Gl 4a,b	↓	↓	↓	1550	187	27,100	↓	↓
Gl 5a,b	↓	↓	↓	1150	359	52,000	↓	↓
Gl 6a,b	↓	↓	↓	1050	259	37,500	↓	↓
LB 75	↓	↓	↓	1050	273	39,700	1.757	↓
LB 78	↓	Thornel 300S	↓	1050	312	45,200	1.829	↓
LB 79	↓	Thornel 300	4000	1050	376	54,600	↓	↓
LB 80	↓	Thornel 300	27.6 MPa	1100	479	69,400	↓	↓
LB 81	↓	Thornel 300	↓	1100	210	30,500	1.780	↓
LB 82	↓	Thornel 300	↓	1100	342	49,600	↓	↓
LB 133	↓	Thornel 300S	2000	1100	↓	↓	1.566	↓
LB 160	↓	↓	13.8 MPa	1120	↓	↓	↓	↓
LB 161	↓	↓	↓	1120	498	72,200	↓	↓
LB 151B	↓	↓	↓	1120	↓	↓	1.700	↓
LB 161C	↓	↓	↓	1120	↓	↓	1.674	↓
LB 161D	↓	↓	↓	1120	↓	↓	1.640	↓
LB 161E	↓	↓	↓	1200	↓	↓	1.675	↓
LB 161F	↓	↓	↓	1200	↓	↓	1.673	↓
LB 162	↓	↓	↓	1120	499	72,500	1.823	↓
LB 163	↓	↓	↓	1120	488	70,800	1.829	↓
LB 134	↓	↓	↓	1100	↓	↓	↓	↓

1. Effect of Amount of Glass in Slurry

In Table VI the effect of the amount of glass in the slurry used to coat the graphite is shown. As can be seen, doubling the glass added to the slurry results in a decrease of strength. Similar tests run with 45 grams of glass in the slurry and 135 grams of glass in the slurry confirm that the best choice seems to be about 85 grams of glass in 200 grams of isopropyl alcohol, 10 grams of polyvinyl alcohol and 5 drops of a wetting agent such as Tergitol's H.D. 527.

2. Effect of Hot Pressing Pressure

The effect of hot pressing pressure on the achieved flexural strength of a Thornel 300 7740 glass composite is shown in Table VII. Doubling the pressure applied to the hot press from 13.8 to 27.6 MPa (2000 to 4000 psi) increases the flexural strength approximately 10%. More importantly, however, it also appears to decrease the scatter shown by the three-point flexural strength data. However, since it has been found that a slight increase in hot pressing temperature achieves much the same result, this is a preferred operational procedure, for at 27.6 MPa (4000 psi) on the unsupported (not filament wound) graphite dies customarily used at UTRC, operation at the higher pressure greatly shortens die life.

3. Effect of Temperature

The effect of temperature on achieved flexural strength of the graphite fiber-glass matrix composite is much greater than the effect of pressure or of the amount of glass present in the slurry. Optical and scanning electron microscopic examination shows exactly what happens as the temperature is increased, and fully explains the data shown in Table VIII. When only the optical micrographs of selected areas of these samples are examined as in Fig. 8, one is unable to sense any significant difference in the samples. However, if one studies the optical tape maps of entire cross sections of the samples (taken at 50X) shown in Figs. 9, 10, 11 and 12, the complete story of what has happened to the samples as the hot pressing temperature is increased from 1025°C to 1100°C is apparent. At 1025°C, Fig. 9, the individual tows are distinct and surrounded by glass rich areas, i.e. they have maintained their individual identity. On the other hand, at 1100°C, Fig. 12, the memories of the individual tows are almost entirely eliminated. Figures 10 and 11, specimens prepared at 1050°C and 1075°C respectively, show intermediate steps in the progression from memories of individual tows to almost complete obliteration of tow identity. This is due to a factor of four change in viscosity of the 7740 glass as the temperature is increased from 1025°C to 1100°C. As shown in Table IX, these results cannot be explained by a variation in the fiber content of the composites.

Table VI

Effect of Amount of Glass in Slurry on Achieved Flexural Strength of Graphite Fiber Reinforced Glass Composite

Specimen	Glass	Fiber	Temp. of Hot Press °C	Pressure psi	3-Point Flexural Strength MPa	3-Point Flexural Strength psi	Glass in Slurry gms	Glass Added Between Layers
LB 75-2	7740	Thornel 300	1050 argon	2000	287	41,700	170	0.11
-3	↓	↓	↓	13.8 MPa	277	40,200	↓	↓
-5				↓	242	35,000		
-6					261	37,800		
-7					271	39,300		
-9					306	44,400		
Average					274	39,700		
LB 78-1	7740	Thornel 300	1050 argon	2000	418	60,600	85	0.063
-2	↓	↓	↓	13.8 MPa	326	47,300	↓	↓
-4				↓	504	73,100		
-5					355	51,500		
-7					456	66,200		
-8					505	73,400		
Average					427.5	63,000		

Table VII

Effect of Hot Pressing Pressure on Achieved Flexural Strength of Graphite Fiber Reinforced Glass Composite

Specimen	Material: Glass	Material: Fiber	Hot Pressing Conditions: Temp. °C	Hot Pressing Conditions: Pressure psi	Achieved 3-Point Flexural Strength: MPa	Achieved 3-Point Flexural Strength: psi	Glass Added Between Layers gms	Glass in Slurry gms
LB 78-1	7740	Thornel 300	1050 Argon	2000	418	60,600	0.063	85
-2				13.8 MPa	326	47,300		
-3					173	25,100		
-4					504	73,100		
-5					355	51,500		
-6					265	38,500		
-7					456	66,200		
-8					506	73,400		
-9					211	30,600		
-10					223	32,300		
-11					304	44,100		
Average					340	49,300		
LB 79-1	7740	Thornel 300	1050 Argon	4000	449	65,080	0.074	85
-2				27.6 MPa	335	48,600		
-3					417	60,500		
-4					No Test			
-5					339	49,200		
-6					460	66,700		
-7					266	38,600		
-8					399	57,900		
-9					345	50,000		
Average					376	54,600		

Table VIII

Effect of Temperature on Achieved Flexural Strength of Graphite Fiber-Glass Composite

Specimen	Material Glass	Material Fiber	Hot Pressing Conditions Temp °C Argon	Hot Pressing Conditions Pressure psi	Density gms/cm^3	Strength on 3 Pt Flexural Test MN/m^2	Strength on 3 Pt Flexural Test x 10^3 psi	Vibrated Die	Glass Added Between Layers gms	Glass in Slurry gms
LB 94										
L-1	7740	Celanese	1025	2000	1.97	414	60.0	yes	0.05	85
L-2				13.8 MPa		330	47.9			
L-3						248	35.9			
C-1						301	43.7			
C-2						291	42.2			
C-3						285	41.3			
R-1						456	66.1			
R-2						418	60.7			
R-3						462	67.0			
					avg	356	51.7			
LB 95										
L-1	7740	Celanese	1050	2000	2.021	265	38.5	yes	0.05	85
L-2				13.8 MPa		218	31.6			
L-3						259	37.6			
C-1						202	29.3			
C-2						199	28.9			
C-3						252	36.5			
R-1						173	25.1			
R-2						215	31.2			
R-3						294	42.6			
					avg	230	33.4			
LB 96										
L-1	7740	Celanese	1075	2000	1.937	295	42.8	yes	0.05	85
L-2				13.8 MPa		274	39.8			
L-3						313	45.4			
C-1						271	39.3			
C-2						268	38.9			
C-3						320	46.4			
R-1						261	37.8			
R-2						302	43.8			
R-3						300	43.5			
					avg	290	42.0			
LB 97										
L-1	7740	Celanese	1100	2000	1.969	399	57.8	yes	0.05	85
L-2				13.8 MPa		411	59.6			
L-3						265	38.4			
C-1						339	49.1			
C-2						340	49.3			
C-3						293	42.5			
R-1						281	40.8			
R-2						362	52.5			
R-3						392	56.8			
					avg	342	49.6			

FIG. 8

OPTICAL MICROGRAPHS OF FOUR UNFRACTURED SAMPLES

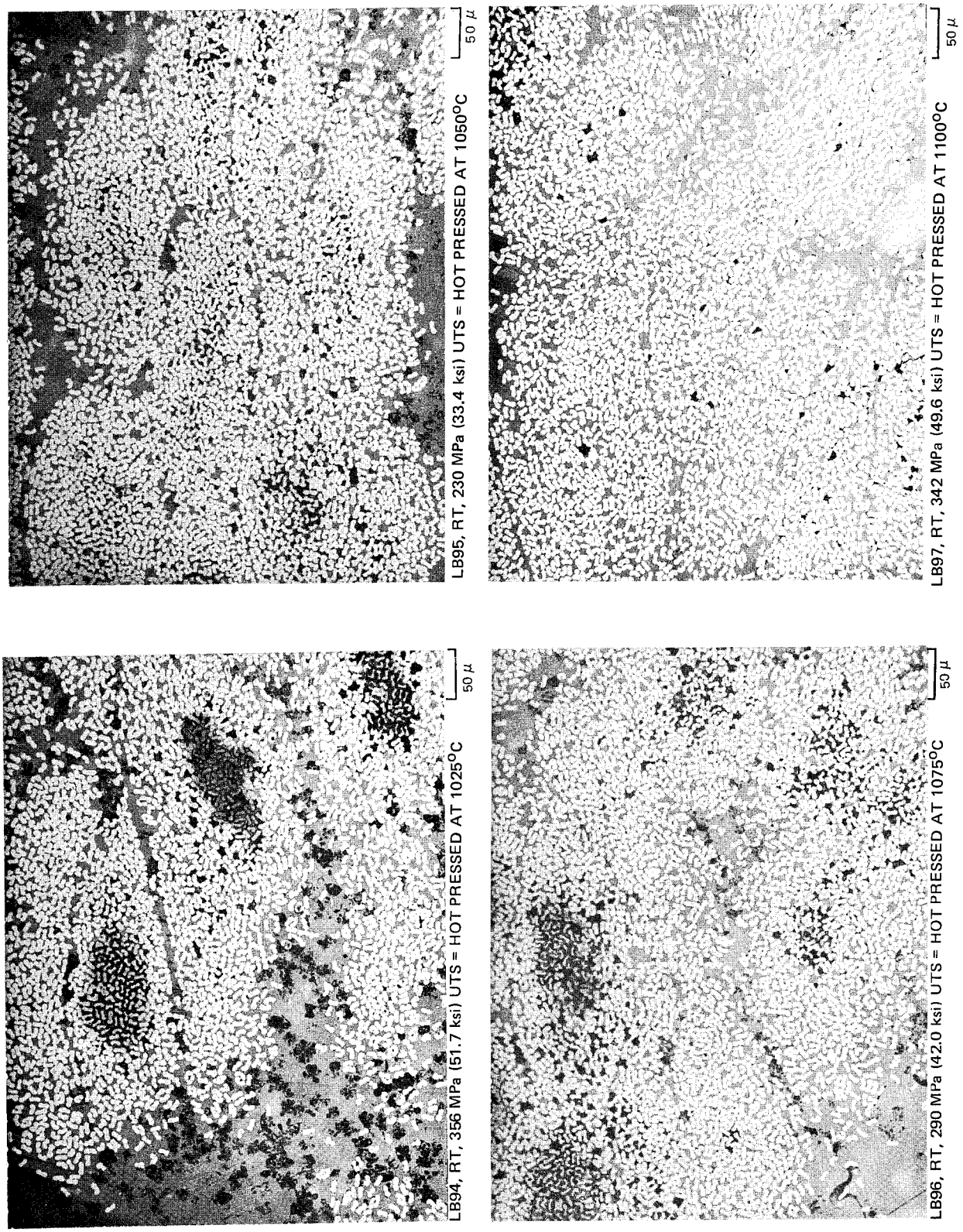
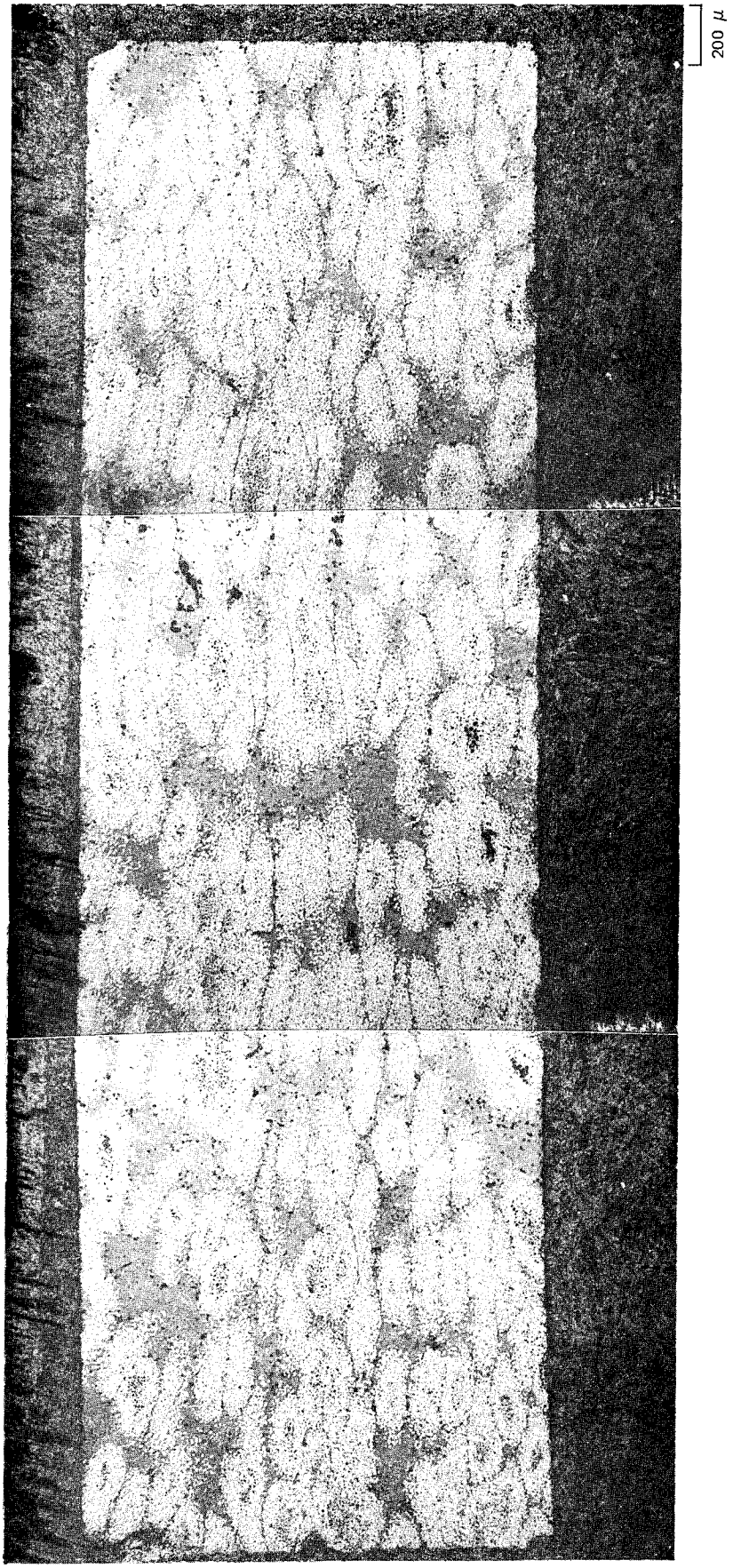


FIG. 9

TAPE MAP OF UNFRACTURED SAMPLE LB94 CELANESE DG–102 FIBER, 7740 GLASS MATRIX, HOT PRESSED AT 1025 °C

76–07–207–1

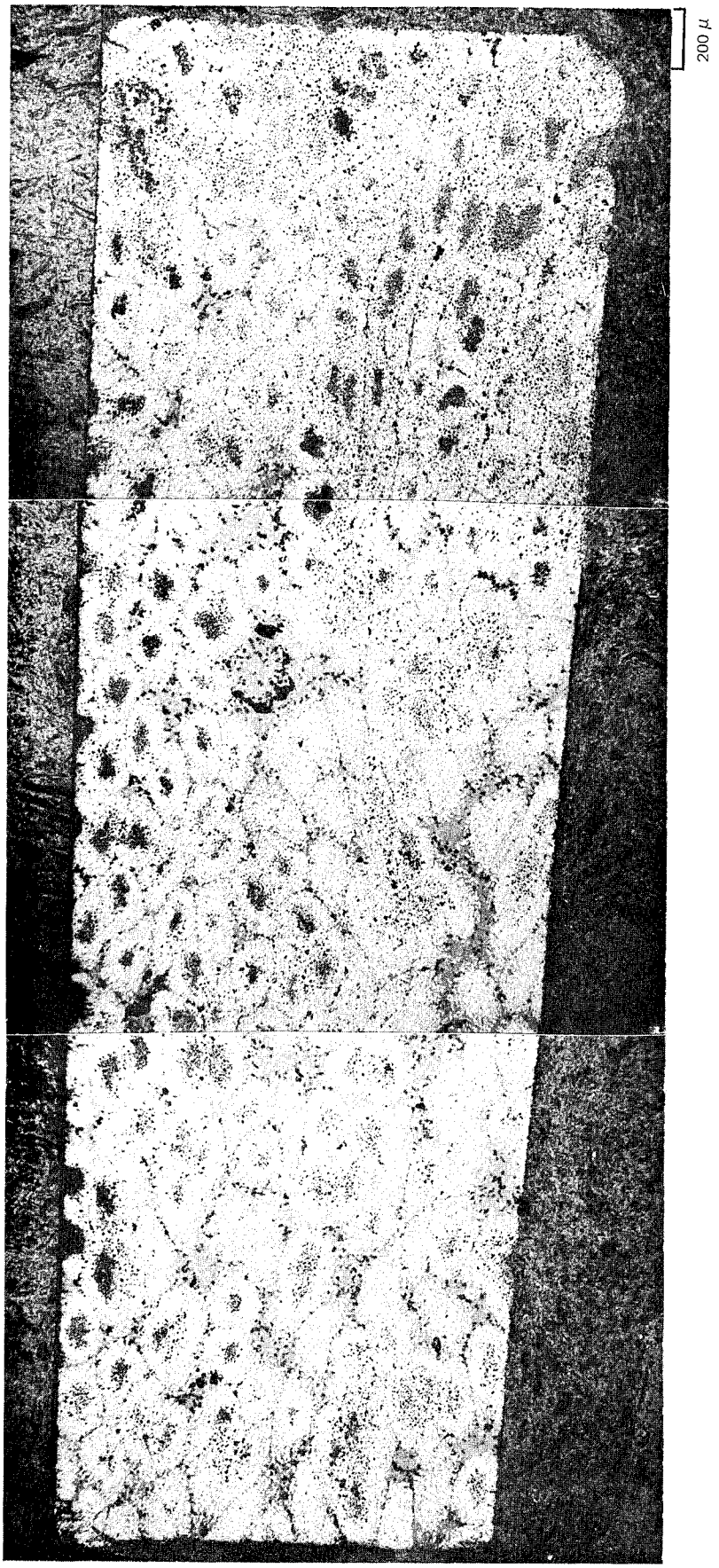
FIG. 10



TAPE–MAP OF UNFRACTURED SAMPLE LB95 CELANESE DG–102 FIBER, 7740 GLASS MATRIX, HOT PRESSED AT 1050 °C

76–07–207–7

FIG. 11



TAPE–MAP OF UNFRACTURED SAMPLE LB96 CELANESE DG–102 FIBER, 7740 GLASS MATRIX, HOT PRESSED AT 1075 °C

76–07–207–5

FIG. 12

TAPE–MAP OF UNFRACTURED SAMPLE LB97 CELANESE DG–102 FIBER, 7740 GLASS MATRIX, HOT PRESSED AT 1100 °C

76–07–207–3

Table IX

Fiber Content and Composite Strength for Several Celanese Graphite Fibers in Corning Glass Works 7740 Glass Matrix Composites

Sample	Glass	Fiber	3 Point Flexural Strength MPa	3 Point Flexural Strength avg, ksi	Density gms/cm^3	*Weight % Carbon	Weight % Glass	Vol % Carbon	Vol % Glass	% Porosity
LB 94	7740	Celanese	356	51.7	1.97	56.5	43.5	56.1	38.0	5.9
95	7740	Celanese	230	33.4	2.021	58.7	41.3	61.4	37.9	0.7
96	7740	Celanese	290	42.0	1.937	55.4	44.6	56.2	39.8	4.0
97	7740	Celanese	342	49.6	1.969	50.8	49.2	52.4	44.6	3.0

*May include residues from polyvinyl alcohol and polystyrene used in sample preparation. All samples were cut from top and bottom surfaces of the same specimen used to prepare nine flexural strength samples. Temperatures of preparation of samples were 1025, 1050, 1075 and 1100°C respectively.

Figures 13, 14, and 15 examine the nature of the fracture surface of these Celanese DG-102 graphite fiber-Pyrex glass specimens prepared at the several temperatures. It is apparent from the scanning electron micrographs that the breaks are fibrous in appearance. Examination of the higher magnification micrographs indicates that the glass is around each and every fiber and tightly bonded to it which as is shown later accounts for the fine environmental stability of these types of composites.

Figure 16 summarizes the joint effects of temperature and pressure. Here the results of three composites made at two different temperatures and two different pressures are plotted on probability paper. It is seen that as the pressure and temperature are increased toward some optimum value, not only does the average three-point flexural strength of the composite increase but the actual spread in individual values of the three-point flexural tests decreases. The approximate linearity of these plots on probability paper indicates that the distribution of three-point flexural values for a given composite is Gaussian in character and that the Gaussian distribution becomes more sharply peaked as we approach optimum hot pressing conditions.

4. Graphite Fiber Effect

Although processing variables such as the temperature and pressure of the hot pressing operation are very important, their influence on the achieved flexural strength of the graphite fiber-glass composite is actually much less than that of the kind of graphite fiber selected to form the composite. In Table X are shown some of the best and more recent results obtained in measuring the three-point bend strength of four types of graphite fiber in 7740 glass matrices. These results may be summarized by saying that at this time the Hercules-HMS graphite fibers in 7740 glass are expected to average higher than 690 MPa or 100,000 psi in three-point flexural strength with corresponding figures of 500 MPa or 72,000 psi for Thornel 300S fiber, 370 MPa or 54,000 psi for Hercules HTS fiber, and 340 MPa or 49,000 psi for Celanese DG-102 fiber. Again as Table X demonstrates there seems to be no valid connection between the modulus and strength of the fiber used and the flexural strength of the composite. It is obvious therefore that the flexural strength of the composite must be dependent on variables not yet properly studied such as the surface chemistry of the fiber and the degree of bonding obtained between a particular kind of fiber and a particular kind of glass.

In the next major section (Section V) of this report the properties achieved with the Hercules HMS fiber in 7740, which gave the strongest composite, and those achieved with the Celanese DG-102 fiber, which is the composite with the greatest environmental stability, are examined in detail. Before concluding this section, therefore, it seems advisable to examine the properties obtained with

FIG. 13

SCANNING ELECTRON MICROGRAPH OF FRACTURE SURFACE
LB95–R3, 294 MPa (42.6 ksi) 1050°C PREPARATION

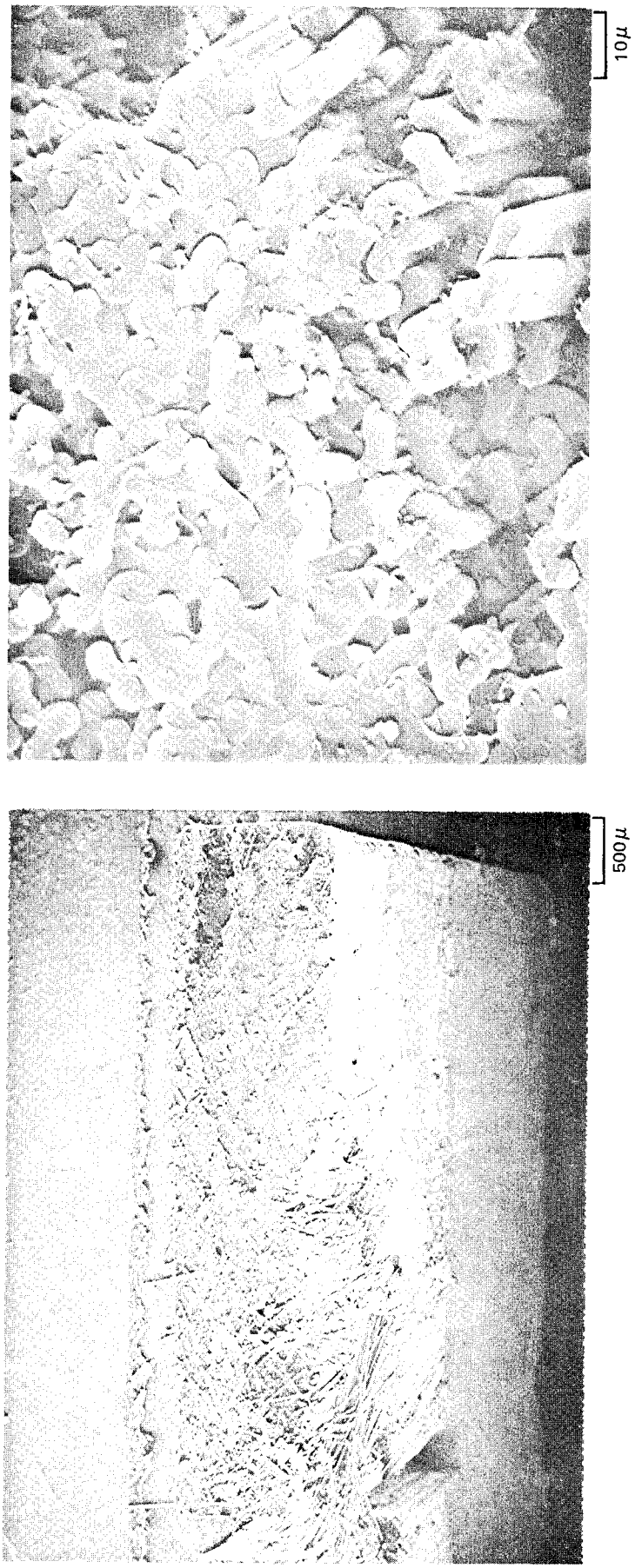
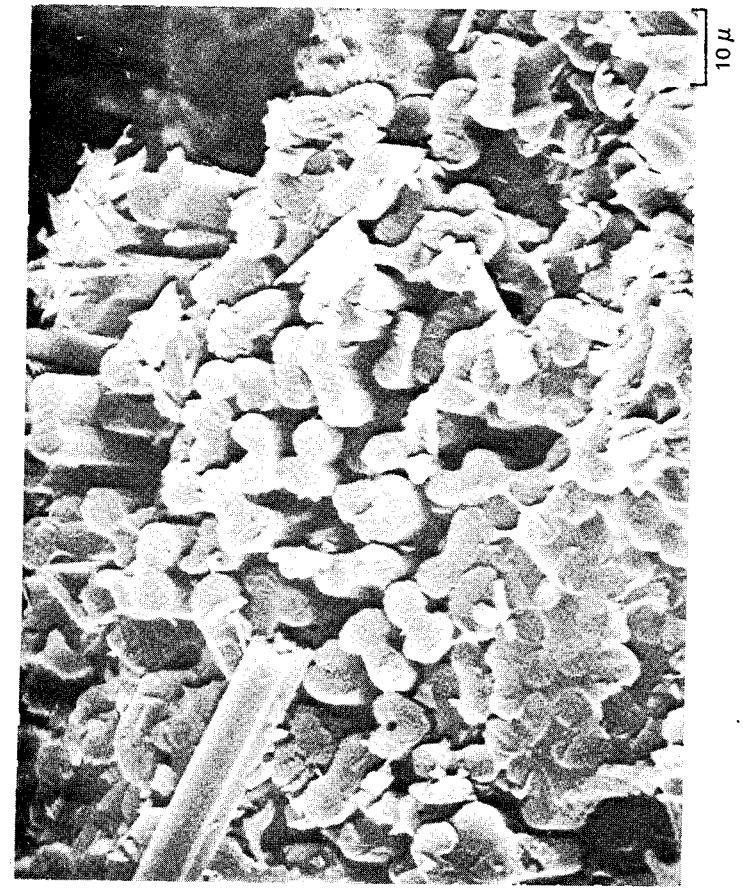
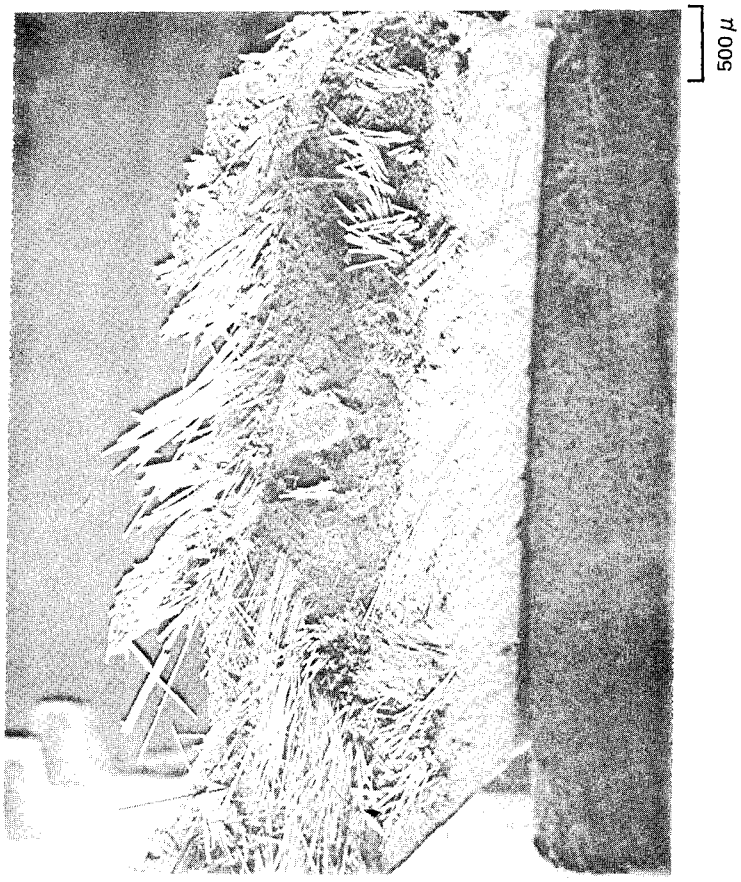


FIG. 14





SCANNING ELECTRON MICROGRAPH OF FRACTURE SURFACE
OF LB96–L2, 274 MPa (39.8 ksi) 1075°C PREPARATION

R77-912545-15

SCANNING ELECTRON MICROGRAPH OF FRACTURED SURFACE OF LB97-L2,
410 MPa (59.6 ksi) 1100°C PREPARATION

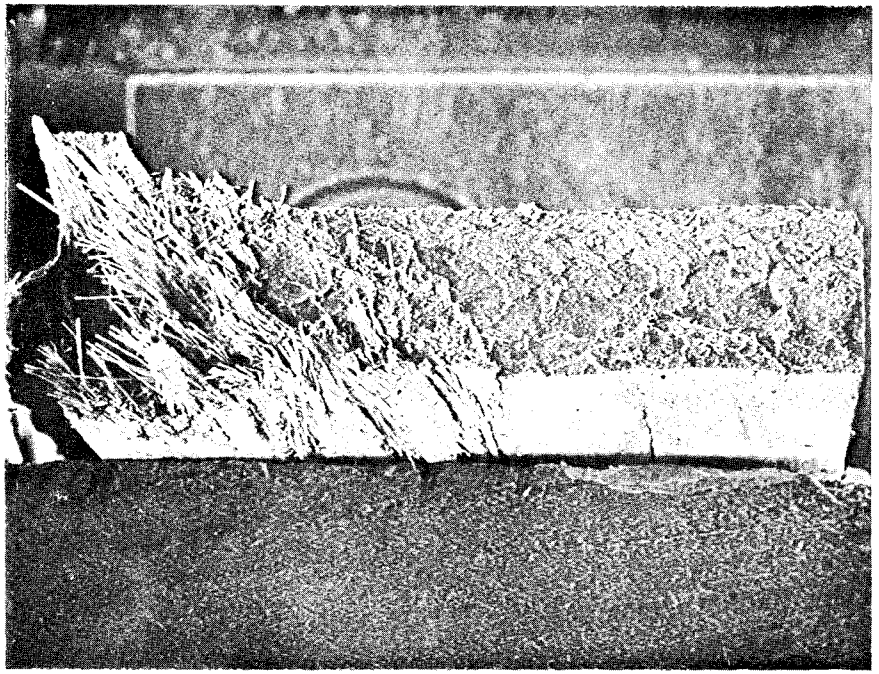
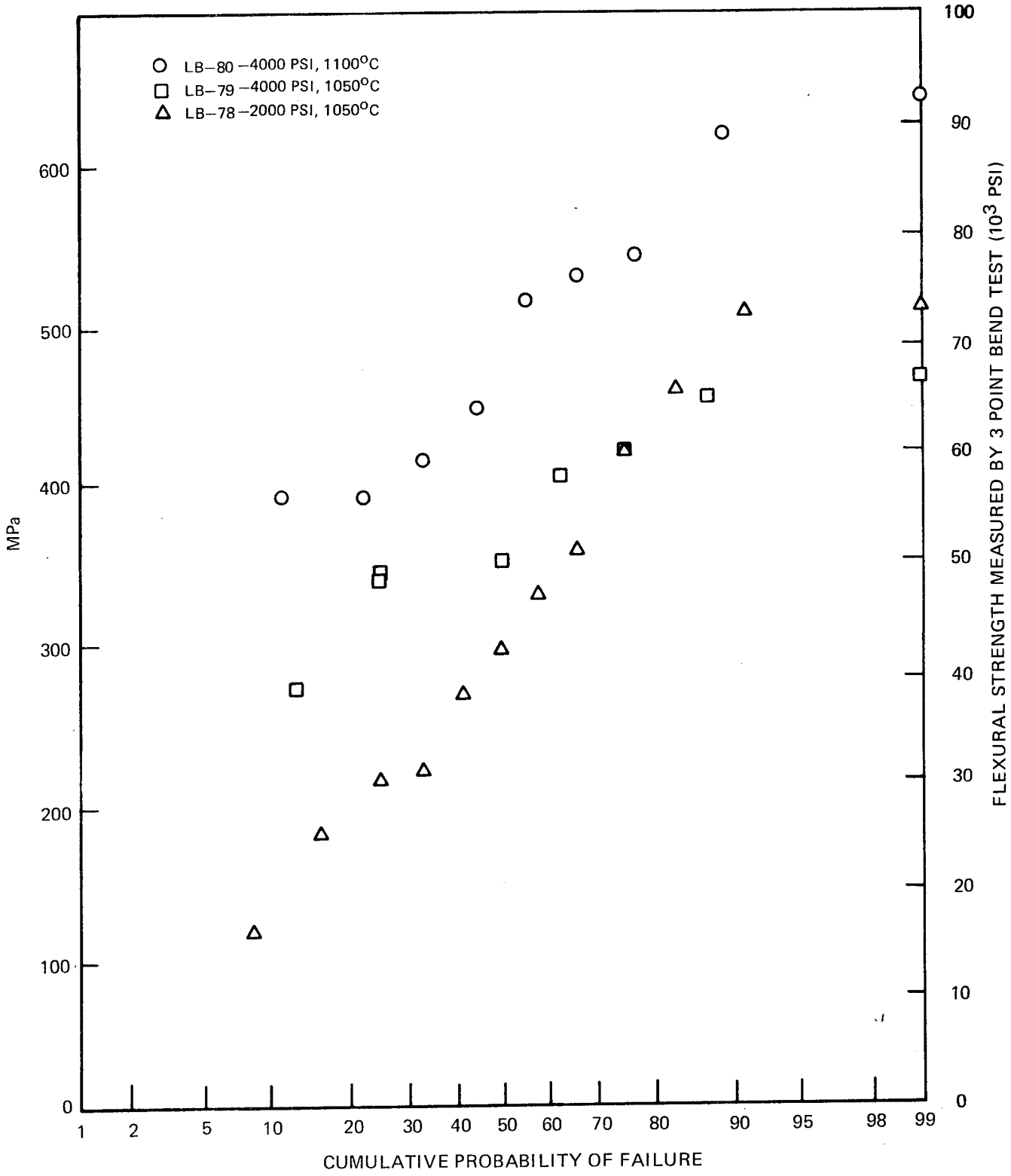


FIG. 15

FIG. 16

DISTRIBUTION OF STRENGTH OF THREE THORNEL 300 FIBER GLASS MATRIX COMPOSITES



76–05–73–1

Table X

Choice of Graphite Fiber and Its Effect on Ultimate Three-Point Flexural Strength of Graphite Fiber-Glass Matrix Composite

Sample Number	Type of Fiber	Fiber Modulus psix10^6	Fiber Strength psix10^3	Number of Fibers in Tow	Glass	Three-Point Flexural Strength MPa	Three-Point Flexural Strength psix10^3
LB 135 RC	Hercules	50.9	392	10,000	7740	673	97.7
CB	HMS	351 GPa	2703 MPa			663	96.2
LC						705	102.0
CC						734	106.0
TC						640	92.9
TR						705	102.0
TL						733	106.0
RL						746	108.0
RB						614	89.0
Average						689	99.98
LB 161 TR	Thornel	33	385	1,000	7740	504	73.1
RC	300S	228 GPa	2655 MPa			397	57.6
RB						516	74.8
TC						474	68.8
CC						528	76.5
CB						556	80.6
TL						467	67.7
LC						522	75.7
LB						519	75.3
Average						498	72.23
LB 148 1	Hercules	37.2	410	10,000	7740	338	49.0
2	HTS	257 GPa	2827 MPa			408	59.2
3						341	49.5
4						357	51.7
5						410	59.4
6						389	56.4
7						408	59.2
8						379	54.9
9						456	66.1
10						354	51.4
11						343	49.8
12						407	59.1
13						319	46.3
14						297	43.0
15						348	50.4
Average						370	53.7

Table X (cont'd)

Sample Number	Type of Fiber	Fiber Modulus psix10^6	Fiber Strength psix10^3	Number of Fibers in Tow	Glass	Three-Point Flexural Strength MPa	Three-Point Flexural Strength psix10^3
LB 97 L1	Celanese	77.0	250	384	7740	399	57.8
L2	DG 102	530 GPa	1724 MPa			411	59.6
L3						265	38.4
C1						339	49.1
C2						340	49.3
C3						293	42.5
R1						281	40.8
R2						362	52.5
R3						392	56.8
Average						342	49.6

the fiber giving the next best result, i.e. Thornel 300 graphite fiber in 7740 glass. In Figs. 17-21 are shown typical optical micrographs of Thornel 300S in 7740 glass. As Figs. 17-19 show, the usual composites made with this material have a very high density of fiber but with a nonuniform distribution with some glass rich areas. This factor may account for the poor high temperature behavior of the Thornel 300 graphite fiber reinforced 7740 glass matrix shown in Table XI where it will be noted that the composite is degraded to about 50% of its original strength when heated in argon at 560°C for 4 hrs and subsequently tested at room temperature and to 25% of its original strength when heated in air for 4 hrs at 560°C. The data obtained for composites made with the Hercules HTS fiber are given in Table X and Fig. 22 as a function of test temperature.

5. Effect of Matrix Composition

The effect of the glass matrix composition on the achieved properties of the graphite fiber reinforced glass matrix composite has received only preliminary study since the C.G.W. 7740 glass seems adequate for a composite whose use temperature, as stated by this contract, is 540°C or 1000°F. The choice of glass matrix composition is, however, important as seen in Table XIII where it is shown that the Hercules HMS graphite fiber used to reinforce a 7740 glass matrix has nearly twice the flexural strength of a Hercules HMS graphite fiber aluminosilicate (C.G.W. 1723) glass matrix.

6. Comparison of Three and Four-Point Flexural Strengths

The effect of span-to-depth ratio on three-point flexural strength was evaluated, over a wide range (20 to 60). The data shown in Table XIV indicate the strength is not a function of the L/D ratio within this range.

The relationship of the three-point flexural strength for these graphite fiber reinforced glass composites to the four-point flexural strength was also evaluated as can be seen in Table XV.

7. High Temperature Limitation on Processing

In Table XVI are shown thermodynamic predictions of reactions which could limit the temperature at which the graphite fiber-reinforced glass composite could be hot pressed. Since thermodynamic considerations merely assure that such reactions can take place and say nothing about the speed with which they occur, it is of interest to investigate the situation experimentally. In

FIG. 17

THORNEL 300S GRAPHITE FIBER IN PYREX GLASS MATRIX TAPE–MAP OF CROSS–SECTION, 50X

77–02–158–3

FIG. 18

OPTICAL MICROGRAPHS OF THORNEL 300 FIBER IN C.G.W. 7740 GLASS MATRIX 200X

LB 79 –As–POLISHED UNFRACTURED SAMPLE

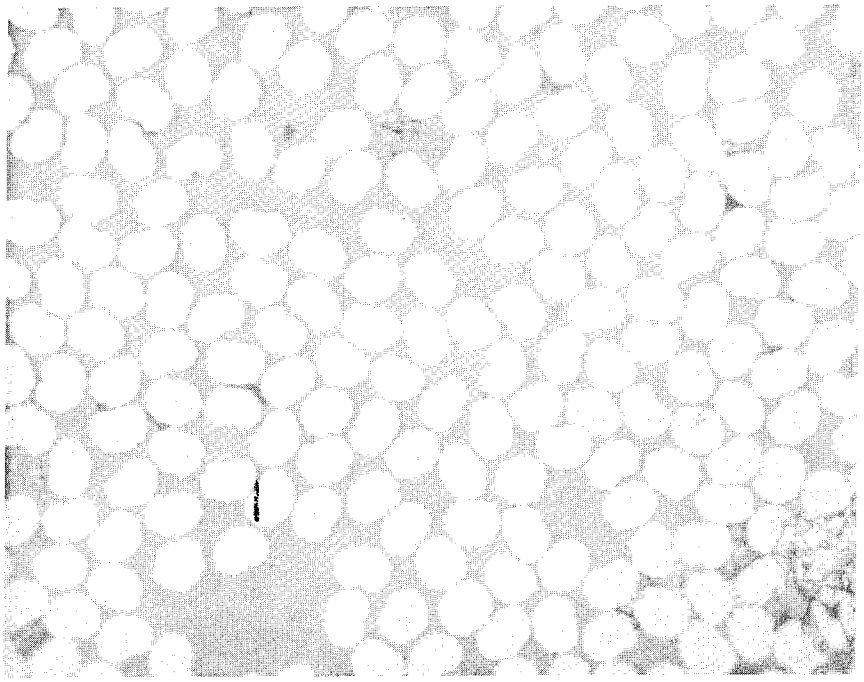
LB 80–CR–ETCHED–FRACTURED SAMPLE

LB 81–ETCHED–UNFRACTURED SAMPLE

76–06–292–5

FIG. 19

THORNEL 300S GRAPHITE FIBER–PYREX GLASS MATRIX CROSS–SECTION PERPENDICULAR TO FIBER DIRECTION



77–02–158–2

FIG. 20

THORNEL 300S GRAPHITE FIBER 7740 GLASS MATRIX CROSS–SECTION PARALLEL TO FIBER DIRECTION

400μ

50μ

77–02–158–1

FIG. 21

TAPE–MAP OF UNFRACTURED SAMPLE LB 81 THORNEL 300 FIBER C.G.W. 7740 GLASS MATRIX

76–06–292–7

Table XI

Elevated Temperature Exposure of Thornel 300S
Graphite Fiber Reinforced 7740

Specimen	Exposure Conditions			20°C 3-Point Bend Strength		Average
	Time	Temp.	Atmosphere	MPa	10^3psi	
LB 163 TC	4 hrs	560°C	Argon	212	30.8	
RC				206	29.9	
RB				248	36.0	
CC				262	38.0	
TL				316	45.9	249 (36.1)
LB 163 TR		none		314	45.5	
CB				501	72.7	
CL				563	81.6	
LB				574	83.2	488 (70.8)
LB 162 TC*	4 hrs	560°C	Air	154	22.3	
CC*				113	16.4	
LC*				112	16.2	
LB*				79	11.4	
RB*				152	22.1	122 (17.7)
LB 162 TR		none		451	65.4	
RC				445	64.6	
CB				528	76.6	
TL				574	83.3	499 (72.4)

*Fibers changed color to white as a result of air anneal

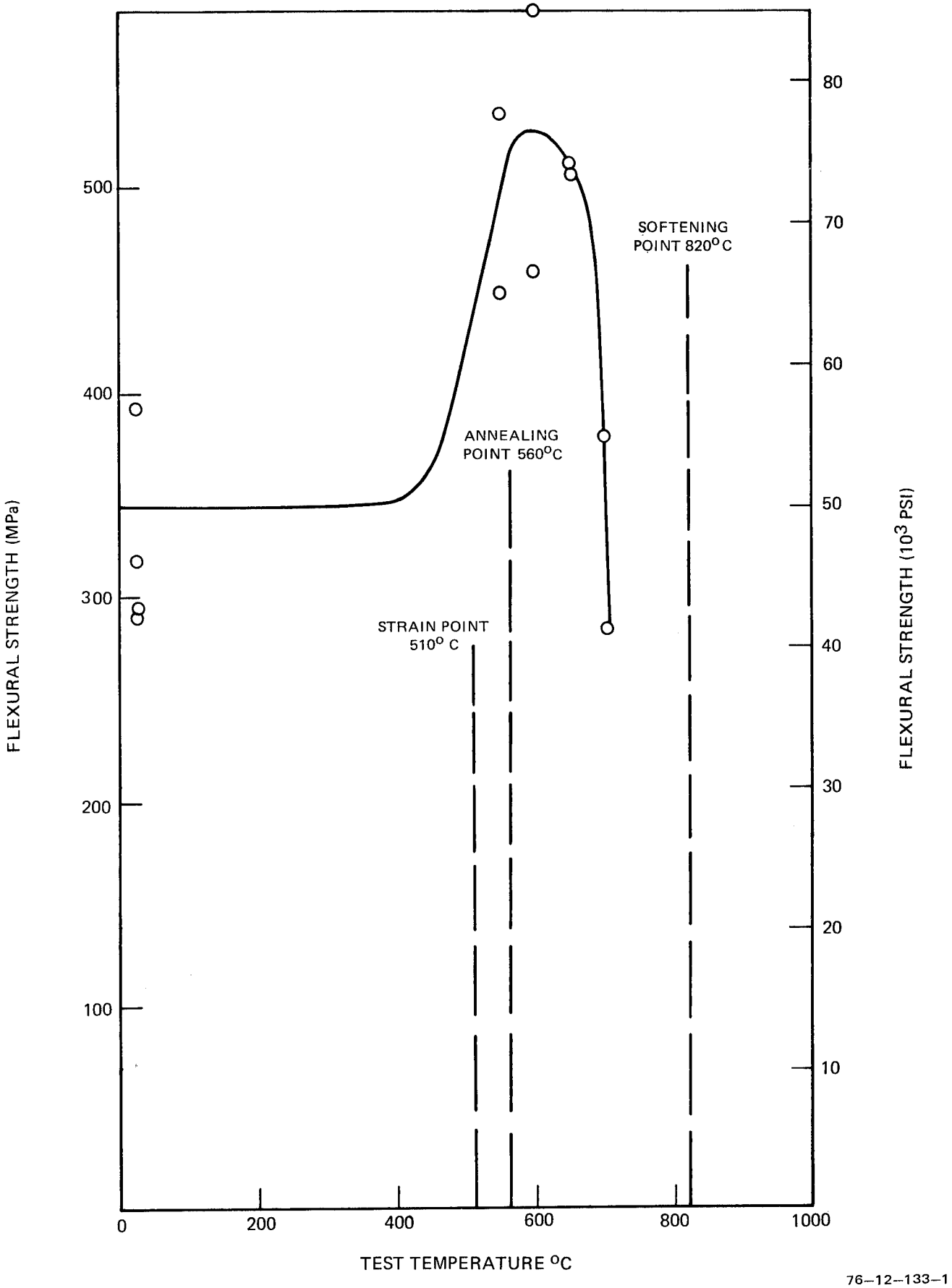
Table XII

Three-Point Bend Strength of Hercules HTS Fiber in C.G.W. 7740 Glass Measured at Elevated Temperatures

Sample No.	Test Temperature °C	3-Point Flexural Strength MPa	3-Point Flexural Strength psi x 10^3
LB 149 CC_1	Room Temp.	352	57.1
CC_2	Room Temp.	318	46.2
BC	Room Temp.	290	42.0
LB	Room Temp.	293	42.5
TL	550	537	77.9
LC_1	550	448	65.0
LC_2	600	459	66.6
TR	600	586	85.0
RC_1	650	511	74.1
RC_2	650	509	73.8
RB	700	379	54.9
TC	700	291	42.2

FIG. 22

FLEXURAL STRENGTH OF HERCULES HTS GRAPHITE FIBER REINFORCED 7740 GLASS MATRIX COMPOSITE AS A FUNCTION OF TEST TEMPERATURE



76–12–133–1

Table XIII

Preliminary Evidence That Choice of Glass Effects the Three-Point Flexural Strength of Graphite Fiber-Glass Matrix Composites

Sample Number	Type of Fiber	Type of Glass	Hot Pressing Conditions		Three-Point Flexural Strength	
			Temp. °C	Press.(psi)	MPa	psi x 10^3
LB 135 RC	Hercules	C.G.W.	1100	2000	673	97.7
CB	HMS	7740		13.79 MPa	663	96.2
LC					705	102.0
CC					734	106.0
TC					640	92.9
TR					705	102.0
TL					733	106.0
RL					746	108.0
RB					614	89.0
Average					689	99.98
LB 172 TR	Hercules	C.G.W.	1120	2000	289	41.9
RC_1	HMS	1723		13.79 MPa	337	48.9
RC_2					324	47.1
RC_3					277	40.2
TC					411	59.6
CC_1					562	81.6
CC_2					not tested	
CB					296	43.0
TL					408	59.1
LC_1					353	51.1
LC_2					299	43.4
LB					371	53.8
Average					357	51.8

Table XIV

Three Point Flexural Strength Values for HTS Graphite in Pyrex Glass Matrix Evaluated at Three L/D Ratios
LB 148

Specimen	Span in.	Thickness in.	L/D	Three Point Flexural Strength MPa	kpsi	Average kpsi
LB 148						
1	1.5	0.025	60	338	49.0	
2		0.025	60	408	59.2	
3		0.024	62.5	341	49.5	
4		0.029	51.7	357	51.7	
5		0.026	57.7	410	59.4	53.8
6		0.064	23.4	389	56.4	
7		0.060	25	408	59.2	
8		0.056	26.8	379	54.9	
9		0.062	24.2	456	66.1	
10		0.062	24.2	354	51.4	57.6
11		0.048	31.25	343	49.8	
12		0.048	31.25	407	59.1	
13		0.048	31.25	319	46.3	
14		0.049	30.6	297	43.0	
15		0.048	31.25	348	50.4	49.7

Table XV

Comparison of 3-Point Bend and 4-Point Bend Test Data for Several Graphite Fiber-Glass Composites

Specimen	3-Point Flexural Strength MPa	3-Point Flexural Strength psi	Strain Gaged 4-Point Flexural Strength MPa	Strain Gaged 4-Point Flexural Strength psi
LB 136 - 3 tests	648	94,000		
- 6 tests			517	75,000
LB 135F - 9 tests	977	142,000		
LB 135G - 9 tests			848	127,300
LB 97 - 9 tests	342	49,600		
LB 97D - 9 tests			309	44,800

Table XVI

Possible Reactions Between SiO_2 and Carbon
at Temperatures Above 1673°K*

1) $SiO_{2(\beta q,\ell)} + 3C \longrightarrow SiC + 2CO_{(g)}$

2) $SiO_{2(\beta q,\ell)} + C \longrightarrow SiO_{(g)} + CO_{(g)}$

3) $SiO_{(g)} + 2C \longrightarrow SiC + CO_{(g)}$

4) $SiO_{(g)} + C \longrightarrow Si_{(\ell)} + CO_{(g)}$

Based on 1st and most important reaction, equilibrium vapors pressures are

Temp (°K)	Equilibrium $P_{CO(atm)}$
1200	1.02×10^{-4}
1400	6.98×10^{-3}
1600	1.62×10^{-1}
1800	1.84
2000	12.4

*Data taken from Bacon, James F., Alex A. Hasapis and James W. Wholley, Jr., Physics & Chemistry of Glasses, Vol. 1, No. 3, June 1960, pp 90-98.

Table XVII the finished weight of the hot-pressed sample is compared with its initial weight as a function of temperature for six Celanese DG-102 graphite fibers in Vycor (C.G.W. 7913) hot-pressed at very high temperatures. The table shows that despite the thermodynamic predictions of reactions at temperatures as low as 1400°C, actual hot pressing operations can be carried out at temperatures of 1600°C for the usual 1 hr dwell time at temperature. Above 1600°C, however, the reactions between glass and fiber make operations impractical. In considering these results it should be noted that the Celanese DG-102 graphite is the fiber with greatest environmental stability and the Vycor glass (C.G.W. 7913) a 96% SiO_2, 3% Al_2O_3 glass is a highly stable glass designed for use at high temperatures.

8. Fabrication in New Hot Press

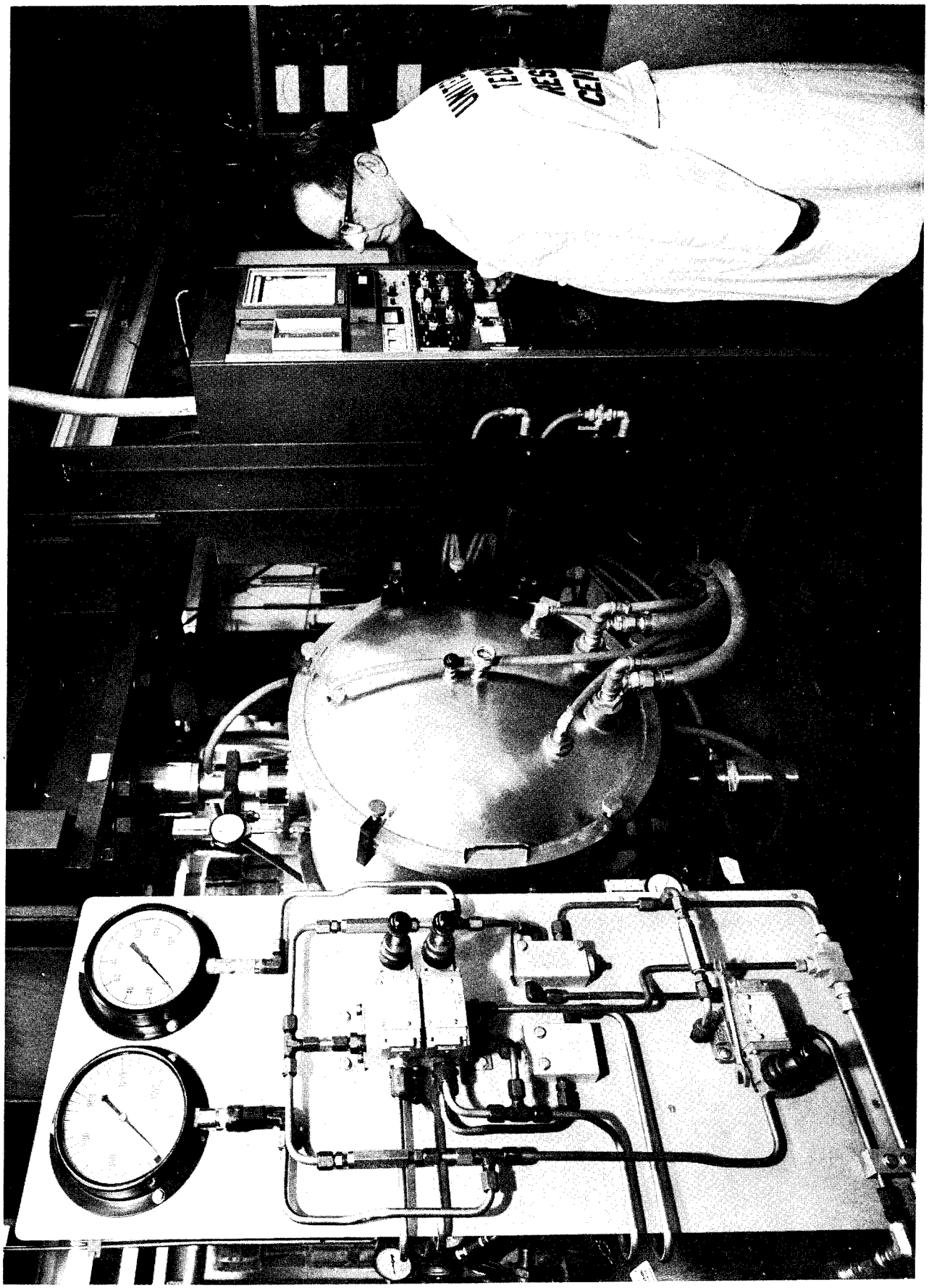
Samples LB 97E,F,G,H,I; LB 135F,G,H,I,J,K,L,M,N,O; LB 148E and F; and LB 161 E and F have been prepared in a new Centorr Hot Press. This equipment is shown in Fig. 23. It permits the fabrication of specimens as large as 6 in. x 4 in. x 1 in. (3 in. thick before pressing) formed with a load up to 60 tons and temperatures of 2100°C in a vacuum of 10^{-6} torr or under argon. This press is double acting in place of the single acting presses used early on this program. With this new press samples were obtained that had greatly improved bending strengths.

Table XVII

Loss in Weight of Celanese DG-102 Graphite Fiber Vycor Glass Composites as a Function of Temperature

Sample	Weight of All Material Before Hot Pressing gms	Finished Weight of Sample After Hot Pressing 1 hr gms	Temperature at Which Hot Pressing Was Performed °C
LB 107	22.55	22.35	1600
LB 108	22.55	15.92	1650
LB 109	22.55	10.64	1700
LB 110	22.55	10.89	1750
LB 111	22.55	9.01	1800
LB 112	22.55	7.14	1850

FIG. 23



NEW CENTORR HOT PRESS AT UTRC

V. PROPERTIES OF TWO SELECTED SYSTEMS

The two most completely characterized graphite fiber reinforced glass matrix composites developed to date are the Hercules HMS graphite fiber in 7740 and the Celanese DG-102 graphite fiber in 7740 composites. The properties obtained thus far for the HMS graphite composites are as follows. An average three-point flexural strength of 977 MPa or 142,000 psi and an average four-point flexural strength (with strain gages) of 848 MPa or 127,300 psi have been measured. These composites have an average modulus of 200 to 206 GPa or 29 to 30 million psi, and a use temperature of 600°C or 1112°F as judged by the fact that the flexural strength in argon increases as the temperature increases from room temperature to 560°C. Very limited thermal cycling and fatigue tests with loads up to 80% UTS, 100 cycles only, show no deterioration in properties for these composites. But the HMS graphite fiber 7740 glass composites do fall to 72% of room temperature strength when heated in air at 560°C for 4 hrs.

On the other hand, the second type of composite which the first year's research has shown to be of major interest is that consisting of Celanese DG-102 fibers reinforcing a 7740 glass matrix. While it is true that at this time the Celanese DG-102 fiber composite has a RT three-point flexural strength of only 342 MPa or 49,600 psi and a four-point flexural strength (with strain gages) of 309 MPa or 49,800 psi it does have a much higher modulus of 303 GPa or 44 million psi. The Celanese DG-102 fiber composite maintains these properties even when heated in air for 4 hrs at 560°C. It is the purpose of this section to examine the basis for these statements in detail.

A. Composites of Hercules HMS Graphite Fiber and 7740 Glass

1. Microstructure

The microstructure of a typical high strength HMS graphite fiber in 7740 glass composite is shown as an optical tape-map of the entire cross section of a test specimen in Fig. 24 and at higher magnification in Fig. 25. The almost unbelievable high density of fiber packing in these samples is immediately visible together with the great uniformity of fiber distribution. Yet, despite the high fiber density the micros lead to the conclusion that each fiber is still completely surrounded by glass with only a few fibers in actual contact with one another. It is believed that this achievement of higher fiber density accounts in part for the strength of these composites.

FIG. 24

OPTICAL TAPE MAP LB135F HERCULES HMS GRAPHITE IN 7740

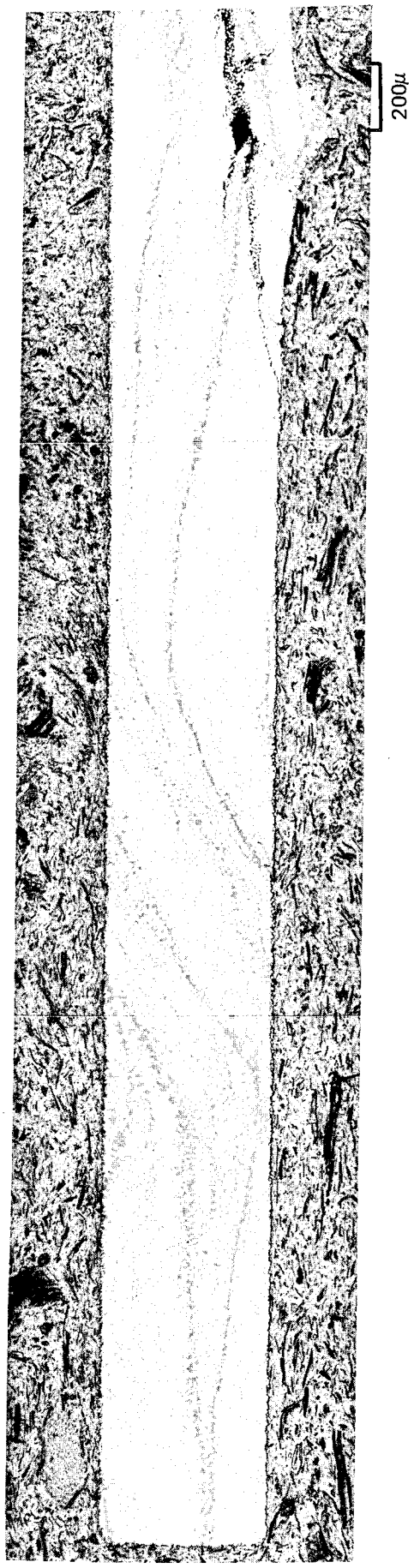
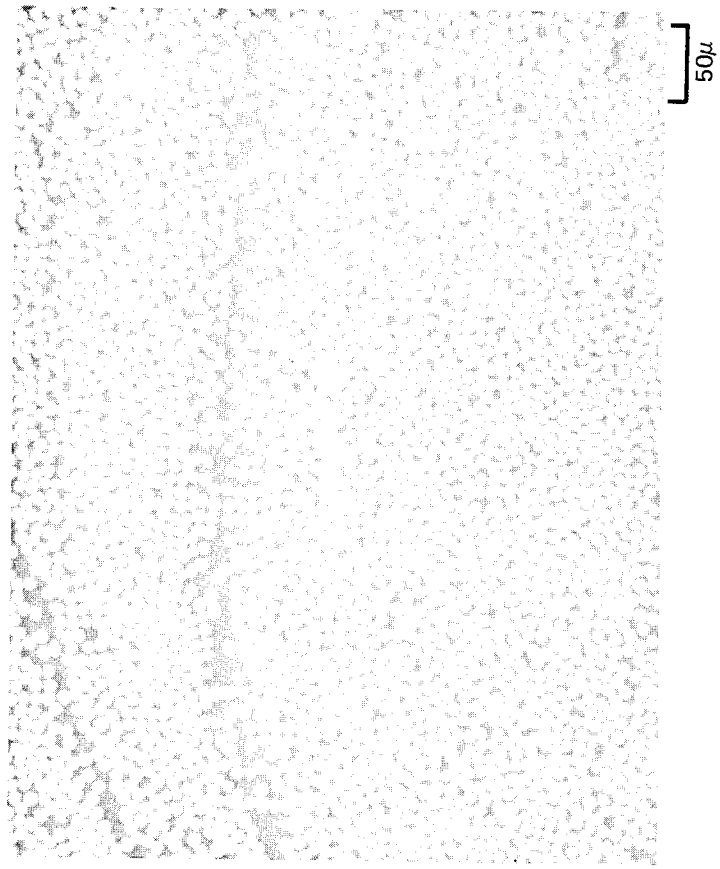
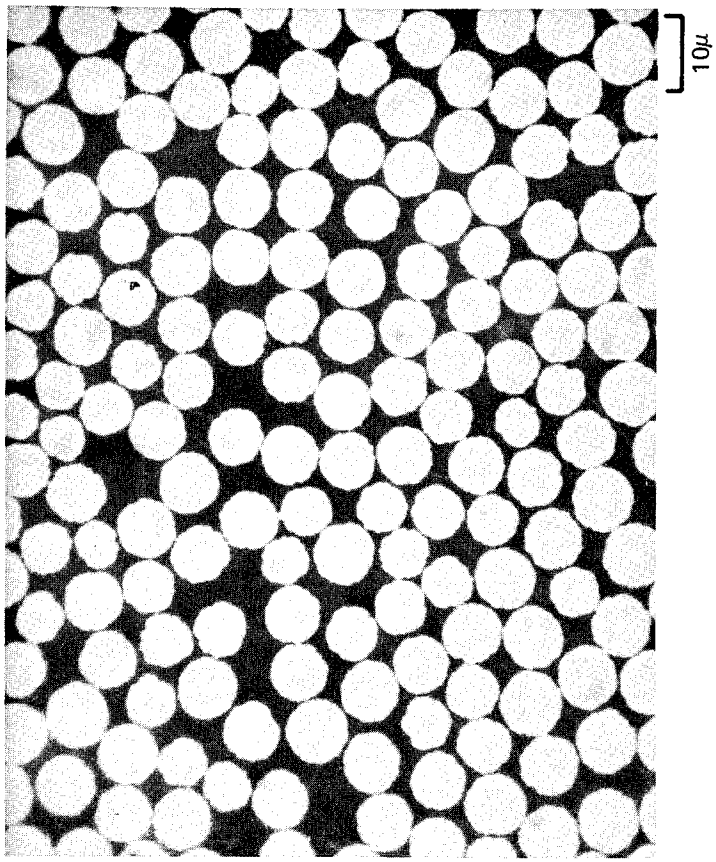


FIG. 25

TYPICAL MICROGRAPHS LB135F HERCULES HMS GRAPHITE FIBER IN 7740





77–07–202–2

2. Flexural Strength

The three-point flexural strength of the best HMS graphite fiber reinforced Pyrex composite made in the UTRC press originally used for this work is shown in Table XVIII and directly below the flexural strength of a similar composite made in the new Centorr press at a slightly higher temperature. While both sets of data show the very high flexural strengths now customarily to be associated with this type of composite, the difference between the two sets of data must be ascribed to factors as yet poorly understood. For example, the new Centorr press is double acting instead of the single action of the press originally used, the later samples are made in new and more tightly fitting dies, the test specimens from the samples were cut by different technicians and on different grinding and cutting equipment, and the two samples were made from different tapes.

However, not only are both samples of Table XVIII high in flexural strength, they also show small standard deviations or a very small spread in test values as can be seen from the plots on probability paper shown in Figs. 26 and 27. Since the linearity of these plots suggests a Gaussian distribution of flexural strengths with small standard deviations, these materials are unique among most brittle materials and can be employed by the designer with a high degree on confidence.

In Table XIX the four-point strain-gaged flexural strength is shown for the second specimen of Hercules HMS graphite fiber reinforced 7740 produced in the new press. The average four-point flexural strength of 876 MPa (127,000 psi) completely corroborated the three-point flexural data reported in Table XVIII for sample LB 135F. The fact that strain gages were used in this measurement as shown in Table XIX also enables one to compute accurate moduli values for this sample and these average 194 GPa or 28.2 million psi. Using the rule of mixtures this would correspond to an approximate fiber content of 47% by volume. The data of Table XIX illustrate that, as might be expected due to the larger volume of specimens experiencing maximum stress in four-point bend, the composite strength is lower for the four-point test than for the three-point test. The average strength of 883 MPa (128,000 psi) is still quite high and failure strains up to 0.42% were recorded.

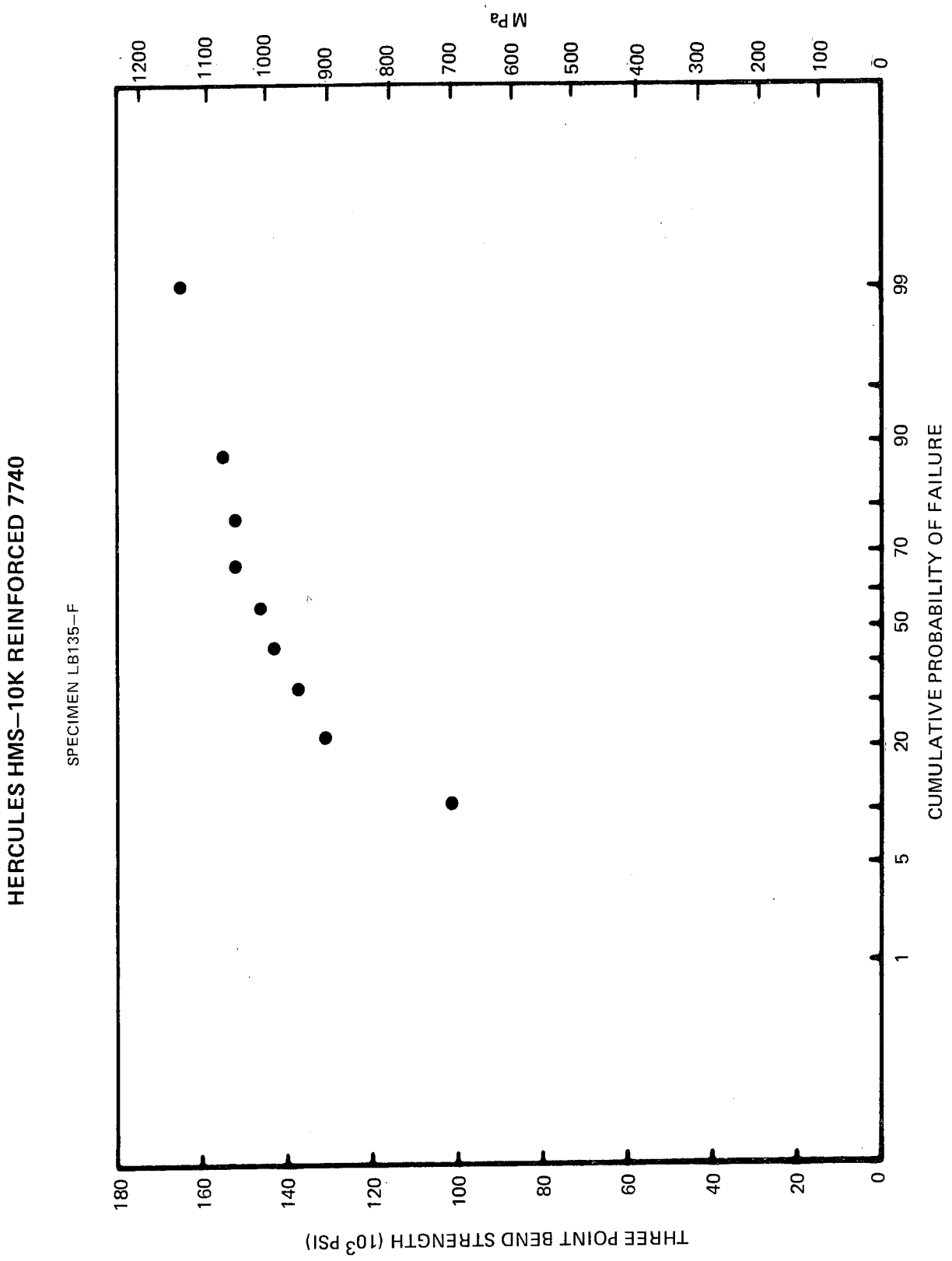
Typical load deflection traces for two specimens taken from another hot pressed HMS graphite fiber in Pyrex sample are shown in Fig. 28. Both totally linear and combined linear - nonlinear deflections were exhibited; however, in all cases specimens did not fracture completely but instead cracks were diverted in the interior of the specimen so that failed specimens remained visibly intact after test. The load strain curves for four-point bend tests on a second HMS fiber Pyrex glass sample are shown in Fig. 29 and represent the two types of

Table XVIII

Flexural Strength of HMS Reinforced 7740

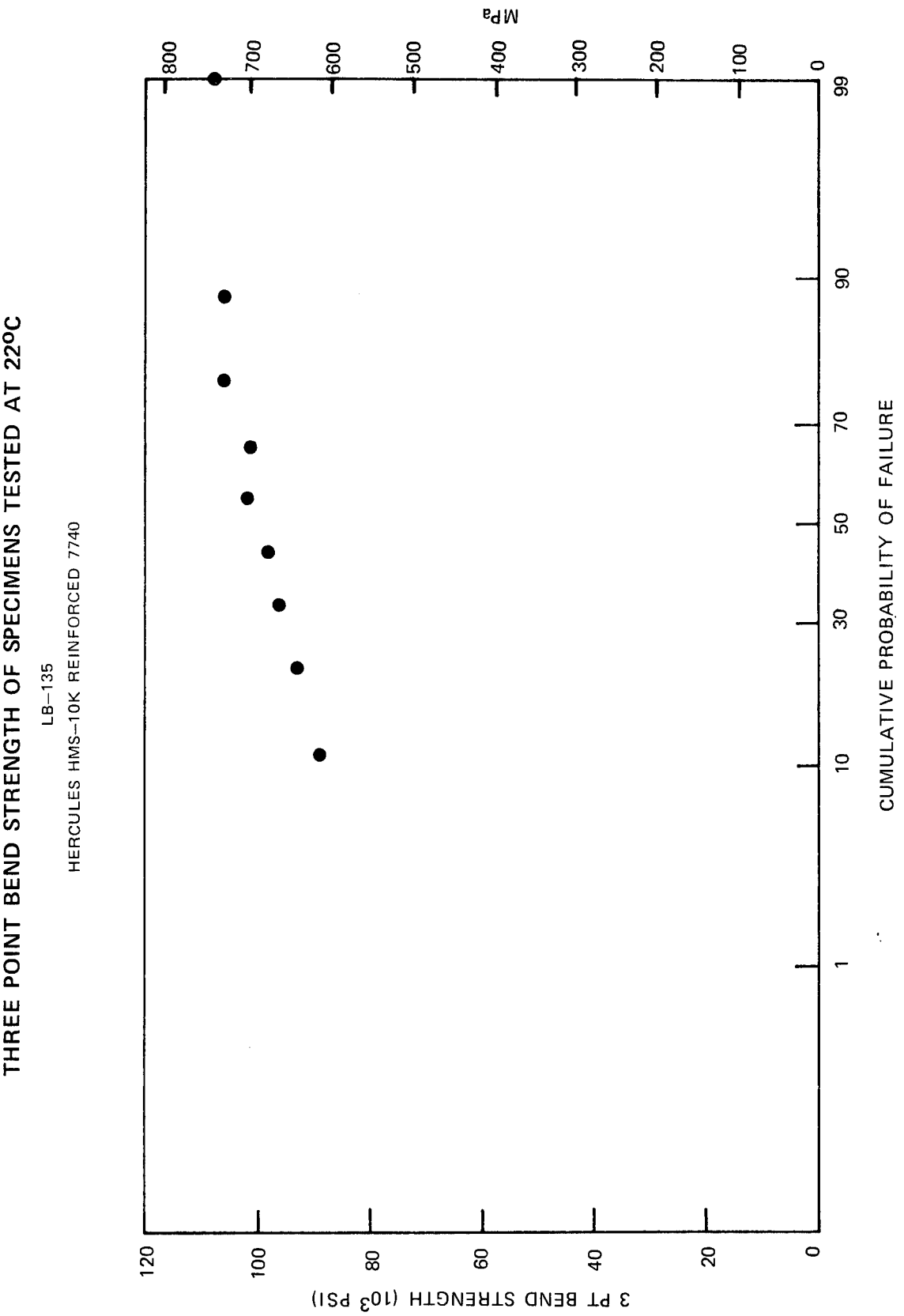
Sample Number	Thickness in.	Hot Pressing Temperature °C	Type of Load Curve	Three-Point Flexural Strength MPa	Three-Point Flexural Strength psi x 10^3
LB 135 RC	0.060	1100		673	97.7
CB	0.056			663	96.2
LC	0.059			705	102.0
CC	0.049			734	106.0
TC	0.032			640	92.9
TR	0.033			705	102.0
TL	0.034			733	106.0
LB	0.033			746	108.0
RB	0.054			614	89.0
			Average	689	99.98
LB 135FRC	0.059	1200		1070	155.0
CB	0.059			1010	146.0
LC	0.068			1050	152.0
CC	0.059			1140	165.0
TC	0.060			903	131.0
TR	0.062			946	137.0
TL	0.063			698	101.0
LB	0.060			1050	152.0
RB	0.061			983	143.0
			Average	977	142.0

FIG. 26



77–05–76–1

FIG. 27



76-10-80-1

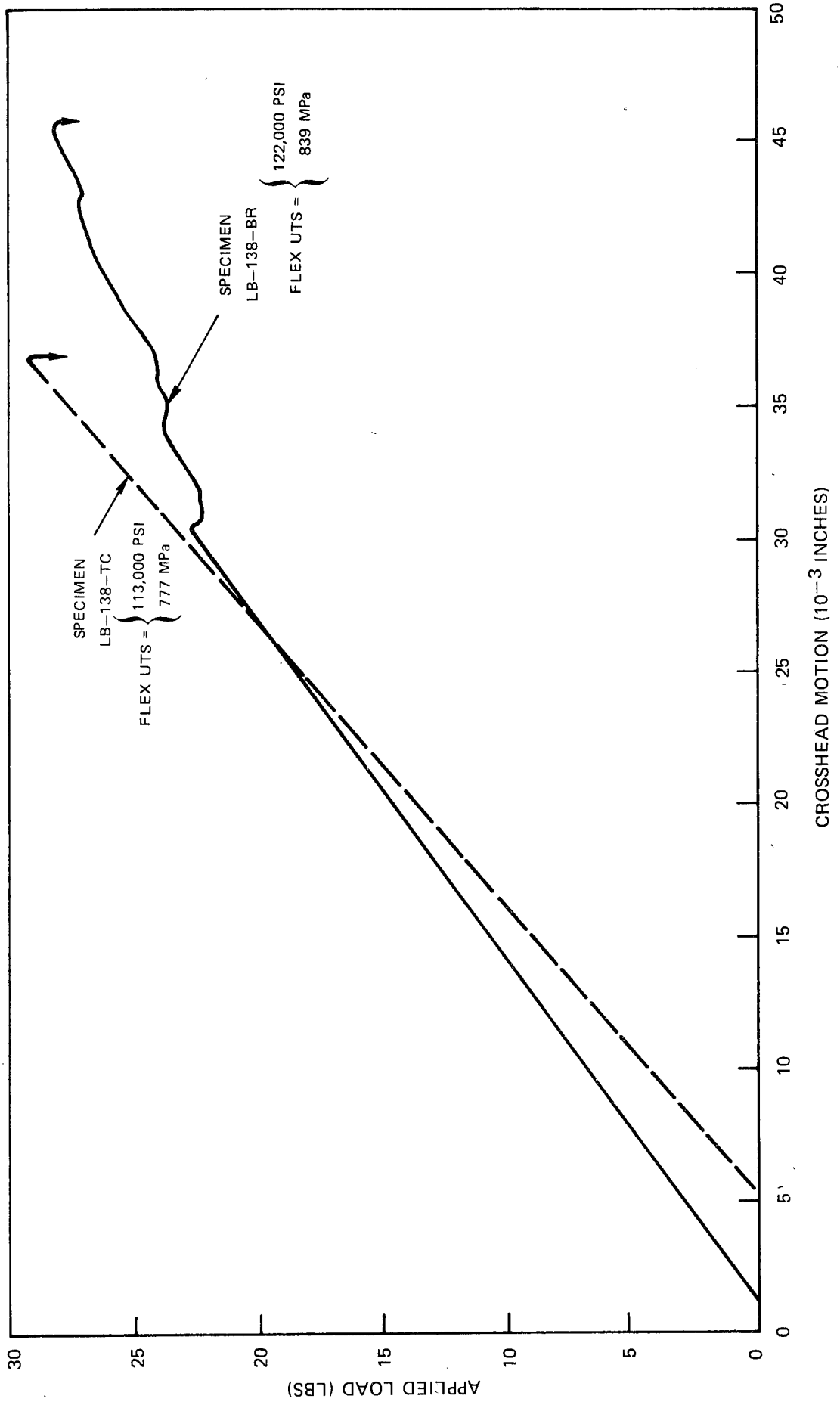
Table XIX

Flexural Properties
HMS Reinforced 7740 Sample LB 135G

4-Point Bend Strength		Elastic Modulus		Strain to Failure
MPa	10^3 psi	GPa	10^6 psi	ε_f
896	130	185	26.8	0.485
938	136	196	28.5	0.477
800	116	201	29.2	0.397
876	127	194	28.2	0.453
878	127			

FIG. 28

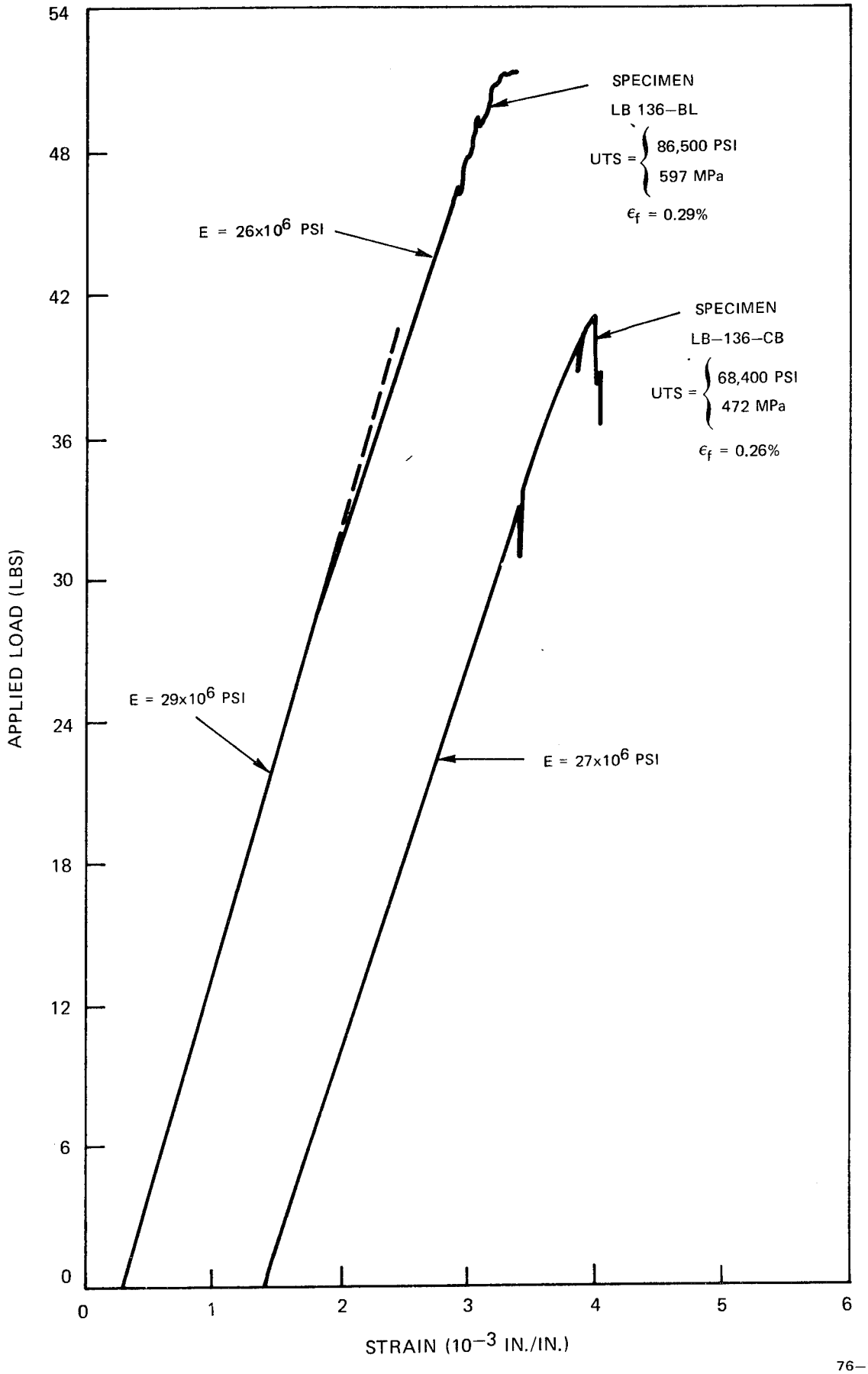
LOAD–DEFLECTION TRACES FOR THE 3–PT BEND TESTS ON
HERCULES HMS–10K REINFORCED 7740



76–10–80–2

FIG. 29

LOAD–STRAIN TRACES FOR THE 4 PT BEND TESTS ON STRAIN GAUGED HERCULES HMS–10K REINFORCED 7740



76–10–80–3

behavior observed. In the case of specimen BL, a nearly bilinear curve was obtained with a secondary elastic modulus 26 x 10^6 psi as compared to the initial value of 29 x 10^6 psi. This type of behavior in composites has often been associated with a transition from elastic-elastic to elastic-plastic regions of fiber-matrix behavior; however, for the current system this transition is unlikely and the operative mechanism is not known. It could be related to some unbonding or matrix fracture mode or it could also be due to some structural defect initiated failure. In contrast, specimen CB demonstrated a linear load-strain trace to failure. It should be noted, however, that there were three major interruptions in this loading curve which resulted in the load dropping off and then recovering. These are indicative of some structural changes in the specimen at regions removed from the strain gage, and thus if viewed from the point of a load vs crosshead displacement curve this specimen would have exhibited a curve like that of specimen BR in Fig. 28. In the four-point test, as well as the three-point test, this material is able to blunt incipient fractures such that the overall specimen can continue to bear load. Also, as in the case of three point bend, all specimens were visibly still intact after fracture, i.e. the cracks were not able to propagate through the whole specimen.

3. Effect of Test Atmosphere on Bend Strength

The environmental stability of this system was also evaluated by exposure to air and argon at 560°C. The data, Table XX, indicate some degradation due to exposure to air. No visible material change could be detected; however, in contrast to the Celanese reinforced 7740 composite, it should be recalled that in this system the fiber does not bond as tightly to the matrix and thus may not be as well protected by the glass. In addition, the higher modulus Celanese fiber, due to its crystallographic orientation, is more oxidation resistant than the somewhat lower modulus Hercules fiber.

4. Comparison of Elastic Modulus

The elastic modulus for HMS reinforced 7740 is compared with values of E_{11} characteristic of other composite systems in Table XXI. The specific modulus comparison given in the last column indicates the superiority of the glass matrix composite.

5. High Temperature Flexural Strength

Composite specimens were tested in three-point bend over a series of temperatures up to 700°C in argon. The resultant data are presented in Fig. 30 and Table XXII. The average strength of 120,000 psi at RT (825 MPa) is higher at 600°C, i.e. 175,000 psi (1213 MPa), and only at 700°C is the deformation of the

Table XX

Elevated Temperature Exposure of Hercules HMS-10K
Graphite Reinforced 7740

Specimen	Exposure Conditions			10^3 psi	
	Time	Temp.	Atmos.		
LB-138	4 hrs	560°C	Argon	78.3	
				82.3	
				86.7	
				113.0	
				90.1	Avg.
LB-138		None		69.6	
				81.1	
				111.0	
				122.0	
				95.9	Avg.
LB-137	4 hrs	560°C	Air	62.1	
				67.6	
				70.2	
				72.1	
				68.0	Avg.
LB-137		None		79.9	
				91.6	
				92.3	
				99.1	
				106.5	
				93.9	Avg.

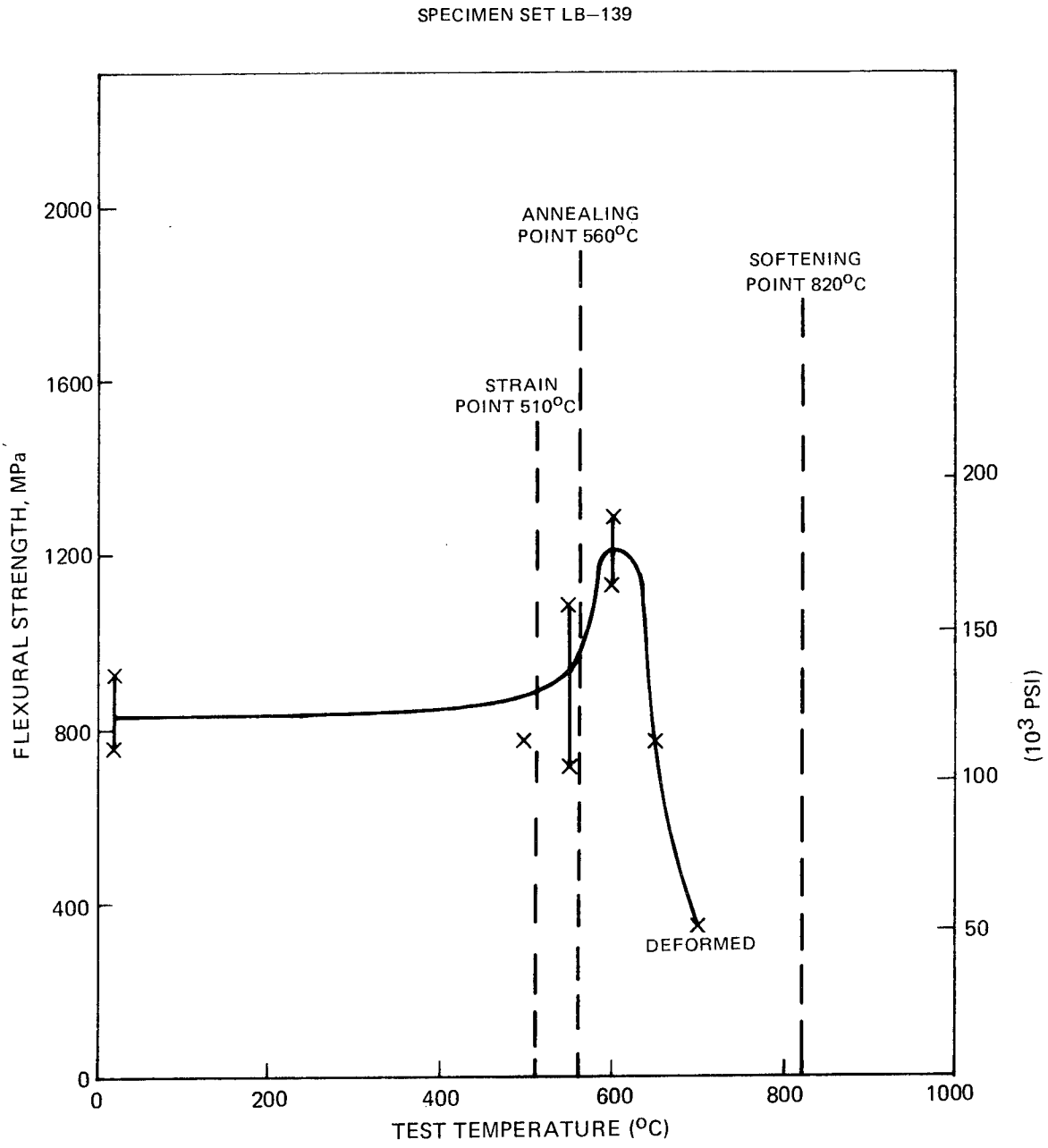
Table XXI

Room Temperature Elastic Modulus Comparison

System with Calculated Fiber Contents	Density ρ (gm/cm^3)	Density ρ ($lb/in.^3$)	Elastic Modulus E_{11} GPa	Elastic Modulus E_{11} 10^6 psi	E_{11}/ρ $10^8/psi/lb/in.^3$
50 v/o Celanese DG-102-7740	2.02	0.072	296	43	5.94
50 v/o HMS-7740	1.98	0.071	193	28	3.94
42 v/o T50-Al	2.30	0.083	207	30	3.61
50 v/o B-Al	2.70	0.097	227	33	3.40
43 v/o B-Ti	3.70	0.133	234	34	2.56

FIG. 30

FLEXURAL STRENGTH OF HERCULES HMS–10K FIBER REINFORCED 7740 GLASS AS A FUNCTION OF TEST TEMPERATURE



76–10–147–1

Table XXII

Hercules HMS-10K Reinforced 7740 LB 139

3 Point Flexural Strength Tested at Temperature in Argon

Test Temperature (°C)	Flexural Strength MPa	Flexural Strength 10^3 psi
22	863	125
22	785	114
500	793	115
550	1081	157
550	706	102
600	1292	187
600	1134	164
650	772	112
700	347*	50.3*

*Specimen highly deformed so that this number is not strictly valid

specimen excessively large. The specimen fractures are shown in Fig. 31 indicating a fibrous nature to the RT fracture surface while at the higher temperatures the specimens delaminated in a limited way. None of these specimens failed completely and a bend fixture had to be used to take the photos shown in Fig. 31 since delaminations are not visible in the unstressed condition.

The load deflection traces for these composites are given in Figs. 32 and 33. A significant transition in load-deflection trace characteristics accompanies the change in fracture appearance noted above.

6. Comparison of High Temperature Strength with that of Other Composite Systems

a. Graphite Reinforced Thermoplastic

The three-point bend data presented in Fig. 34 have recently been obtained for a NASA sponsored program at UTRC*. The fiber is the same Hercules HMS fiber used on this program to reinforce 7740. Note the following points in comparison with Fig. 30.

The resin matrix composite maximum flexural strength at room temperature is approximately equal to the strength of the HMS-7740 at 600°C, although greater at room temperature.

The rate of strength decrease in the vicinity of the resin glass transition temperature is rapid, as it is for the glass matrix composite above 650°C.

b. Graphite Reinforced Aluminum

The only flexural strength data for graphite reinforced aluminum the authors could find was recently published by W. Harrigan of Aerospace Corporation. These data, for wire and plates, are presented in Fig. 35 as a function of test temperature and compared with the data of Fig. 30.

*Novak, R. C., Graphite Fiber Reinforced Thermoplastic Resins, NAS3-20077, CR-135196, 1976.

FIG. 31

HMS–7740 THREE POINT FLEXURAL TEST SPECIMENS

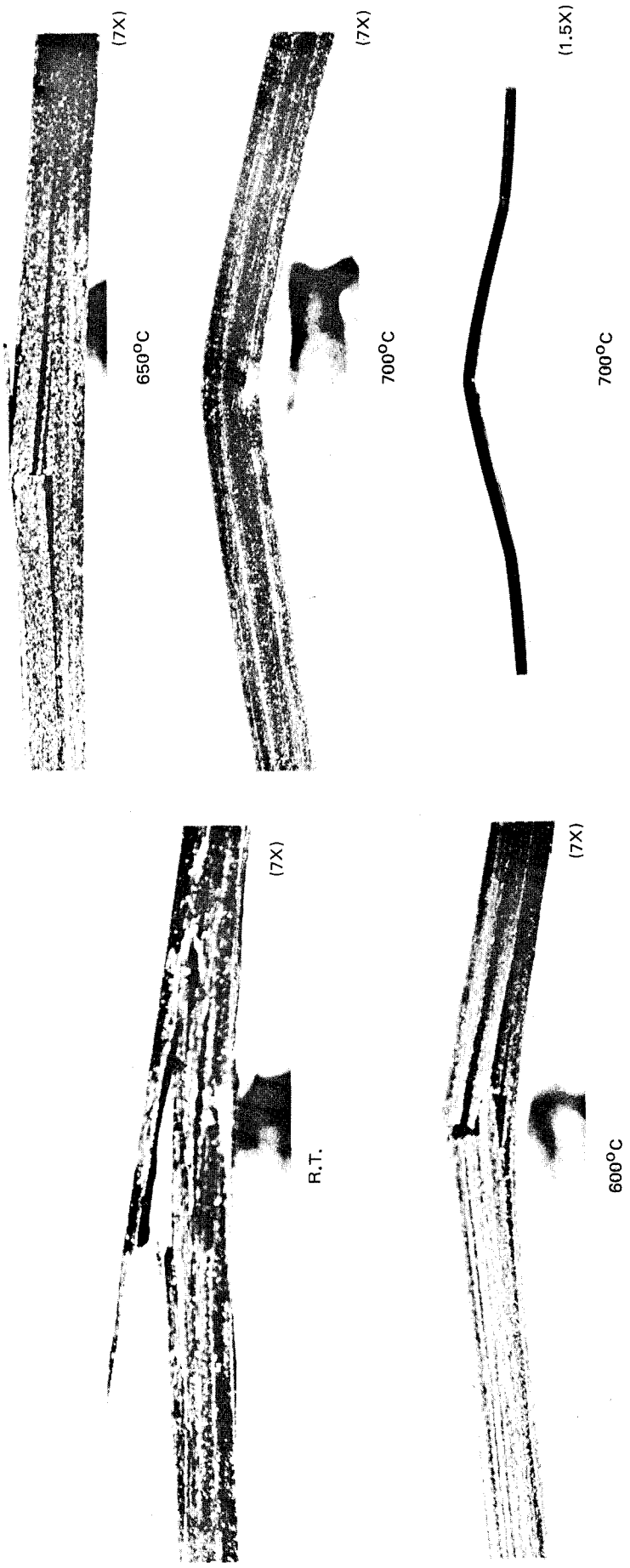
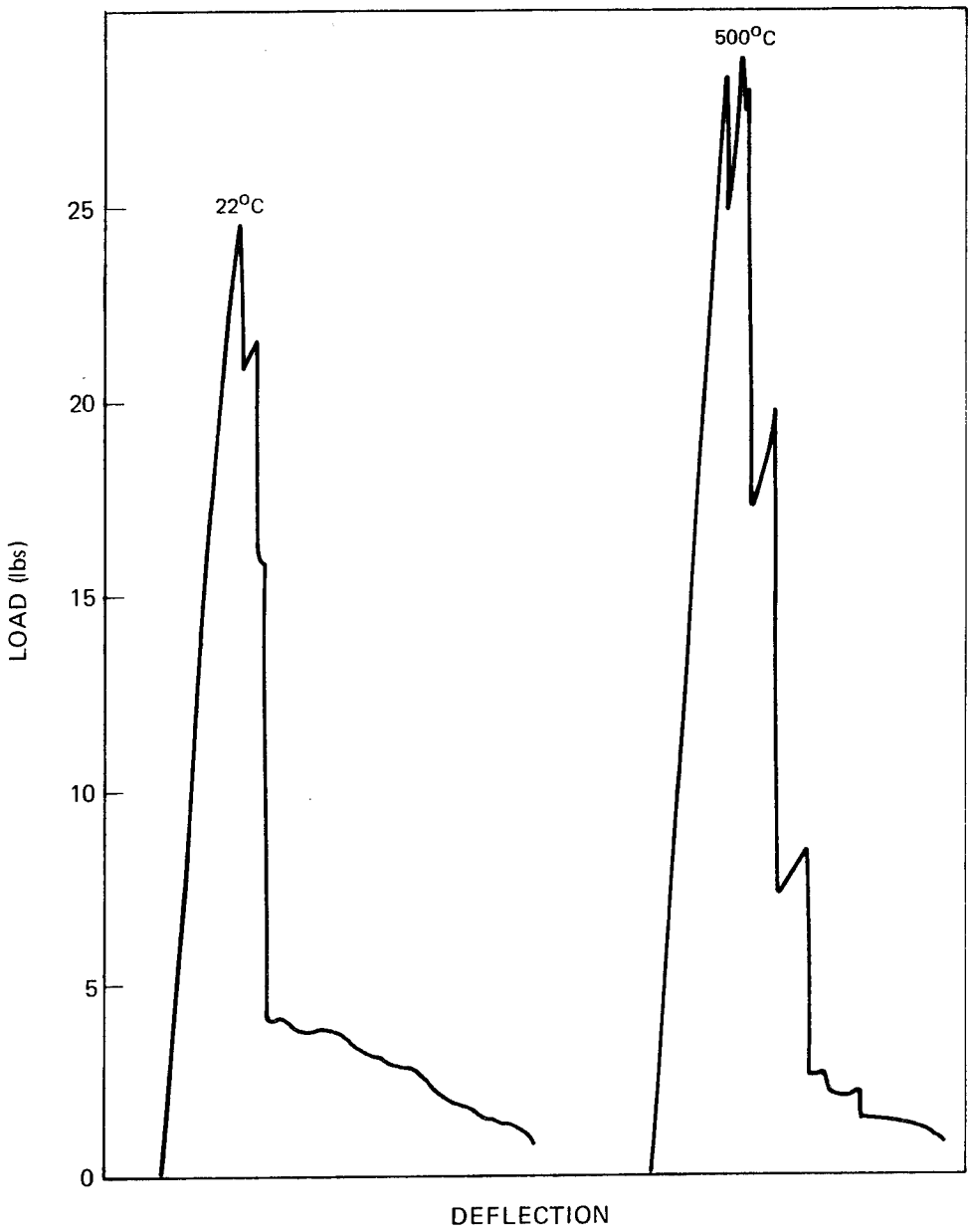


FIG. 32

HERCULES HMS–10K REINFORCED 7740

LB–139

3 PT BEND AT TEMPERATURE



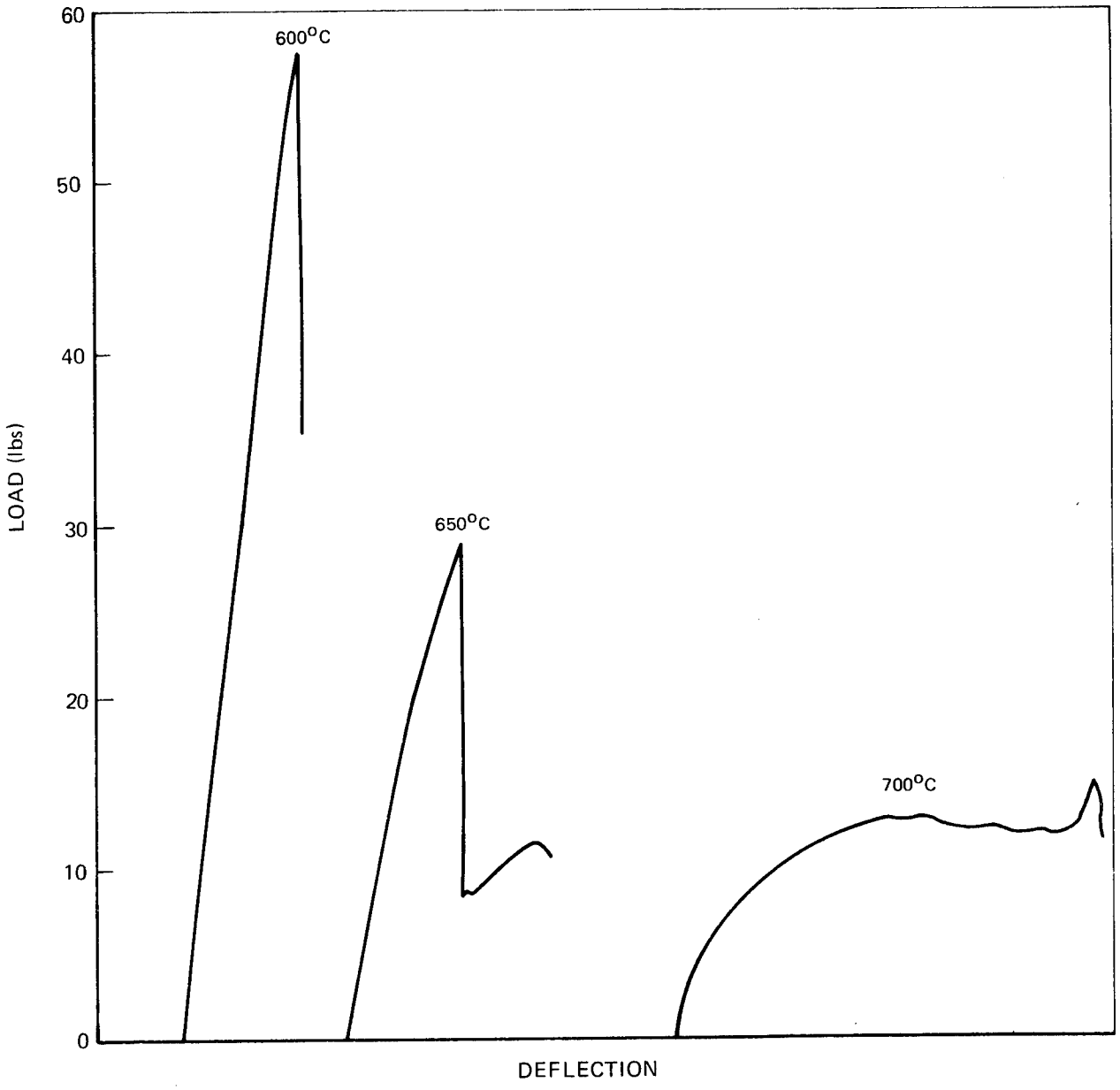
76–10–147–2

FIG. 33

HERCULES HMS–10K REINFORCED 7740

LB–139

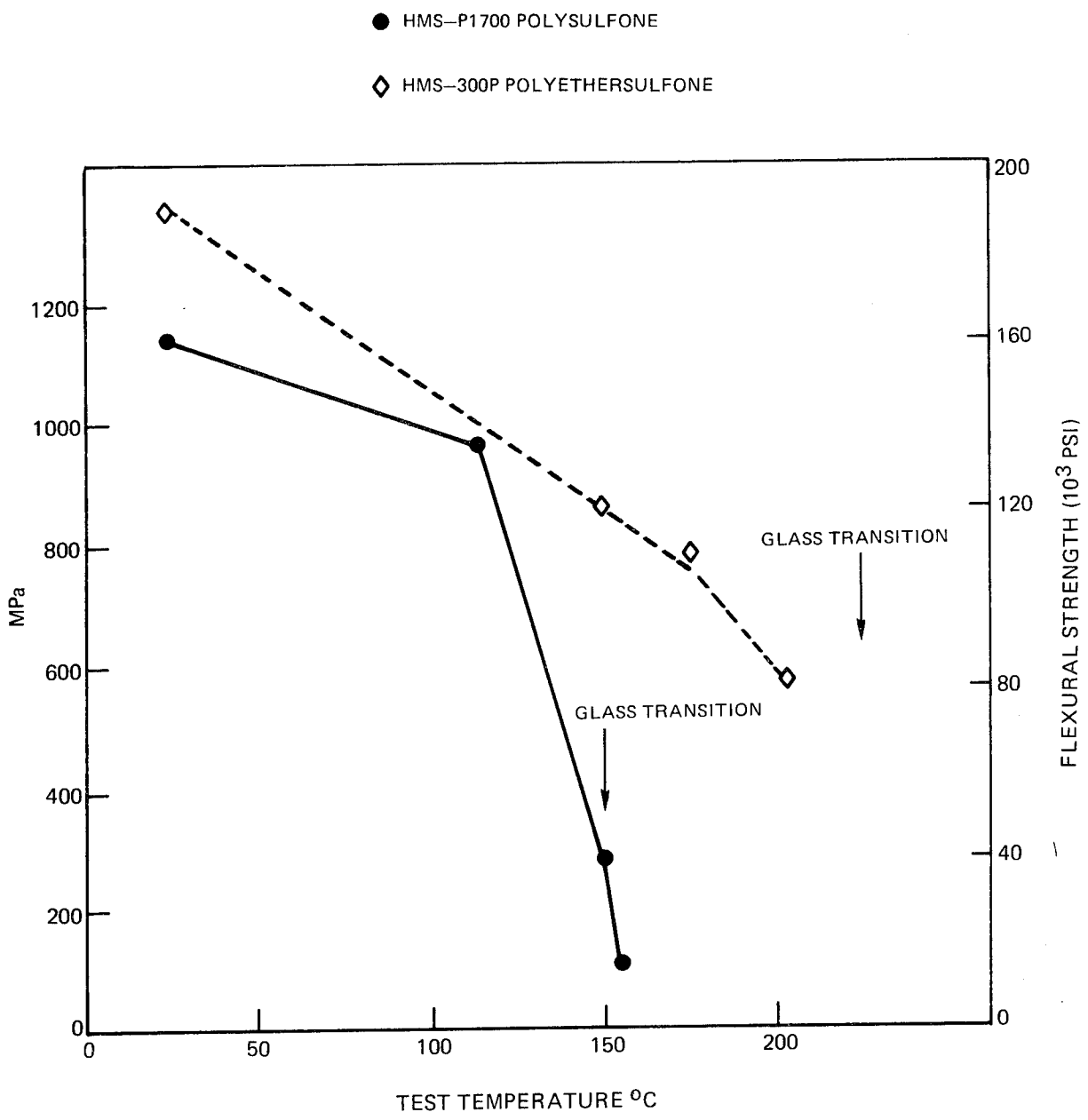
3 PT BEND AT TEMPERATURE



76–10–147–3

FIG. 34

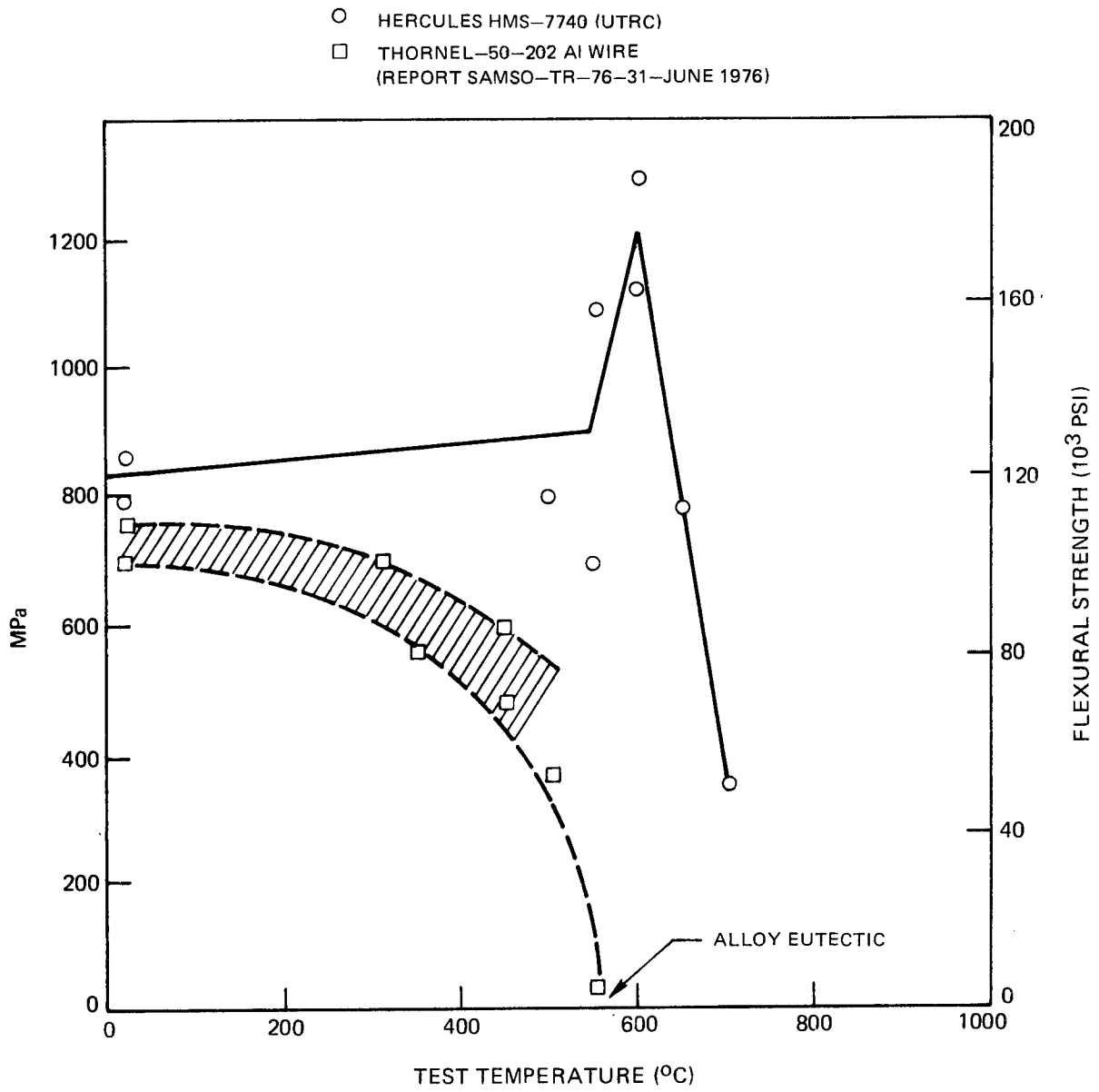
FLEXURAL STRENGTH OF HERCULES HMS–10K FIBER REINFORCED 7740 THERMOPLASTICS AS A FUNCTION OF TEST TEMPERATURE*



* UTRC CONTRACT NAS3–20077, 1976

76–11–107–5

FLEXURAL STRENGTH COMPARISON



76–11–107–6

- Over the entire test temperature range, the glass matrix composite is equal to or superior to the aluminum matrix composite in strength.

- On a specific property basis the glass matrix composite would offer an additional advantage which in this case would be significant. The density of the aluminum matrix composite is approximately 2.4 grams per cubic centimeter while that of the HMS-7740 is approximately 2.0 grams per cubic centimeter. The specific strength comparison is given in Fig. 36.

- The maximum use temperature of the glass matrix composite should be significantly greater than that of the graphite aluminum.

c. Borsic Reinforced Ti-6Al-4V

This is the only metal matrix composite with a plausible use temperature in the range of RT-500°C (excluding reinforced high temperature superalloys which have a much higher density). Therefore, the comparison with this system at temperatures above 300°C is very meaningful. The data are presented in Fig. 37. In this case flexural data over the temperature range of interest are not available so Borsic-Ti tensile test data were used. To make a more realistic comparison, the Borsic-Ti composite tensile data were multiplied by a factor of 1.4 which, in the past at UTRC, has been shown to be the ratio of flexural strength to tensile strength at room temperature for Borsic-Ti. In addition, the data were divided by composite density to obtain the specific flexural strength comparison shown in Fig. 38. At temperatures above 150°C the glass matrix composite is clearly superior to the titanium matrix composite.

7. Fracture Tougnness Testing

Notched three point bend specimens were fabricated and tested in an attempt to characterize the fracture toughness of this composite system. The specimen geometry is given in Fig. 39 and specimen dimensions with resultant data are given in Table XXIII.

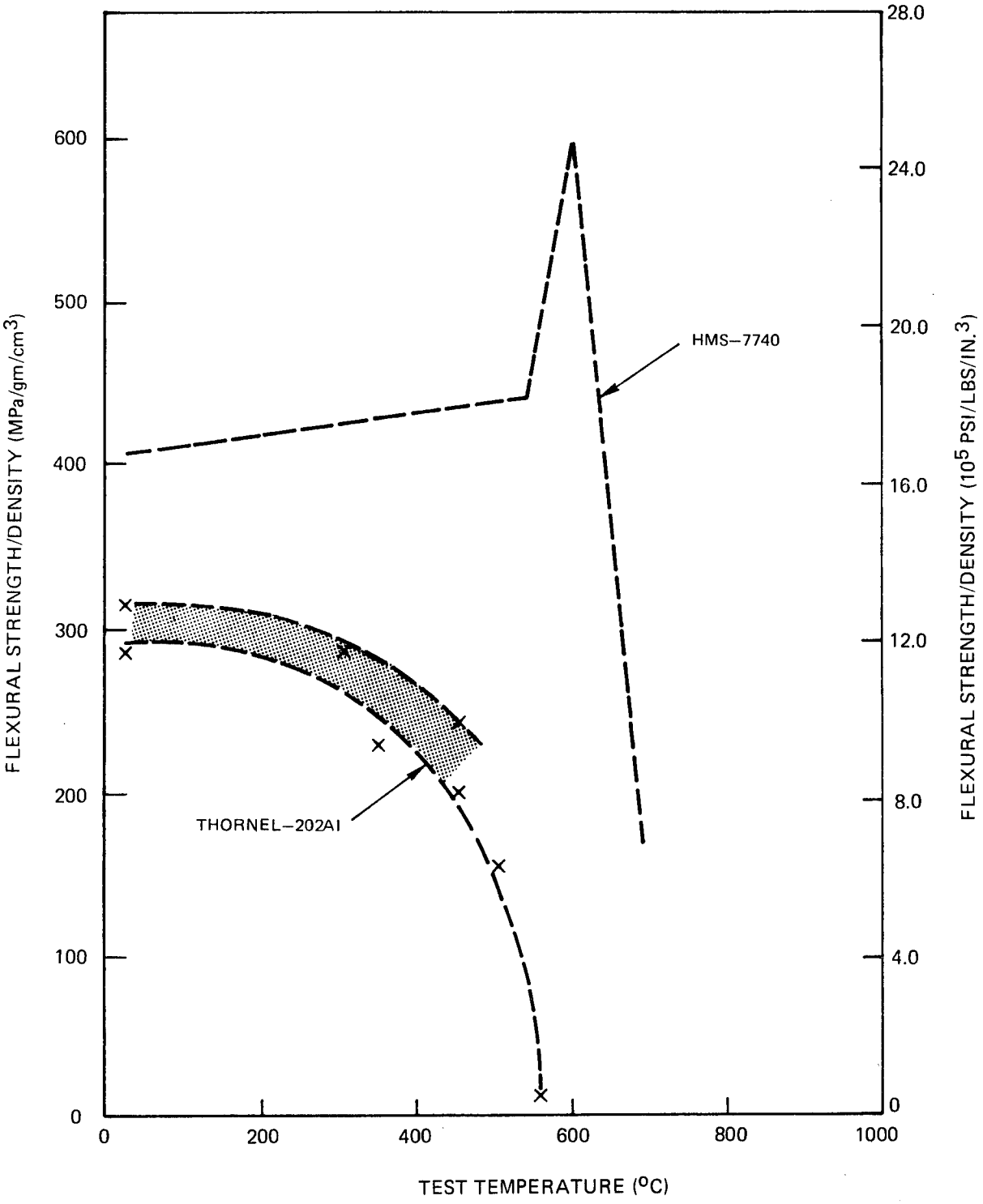
Two types of mechanical test procedures were used.

- Specimen 140-2 was tested in slow 3 point bend at room temperature.

- The other three specimens were tested using the UTRC instrumented impact testing machine which is capable of operating at elevated temperatures.

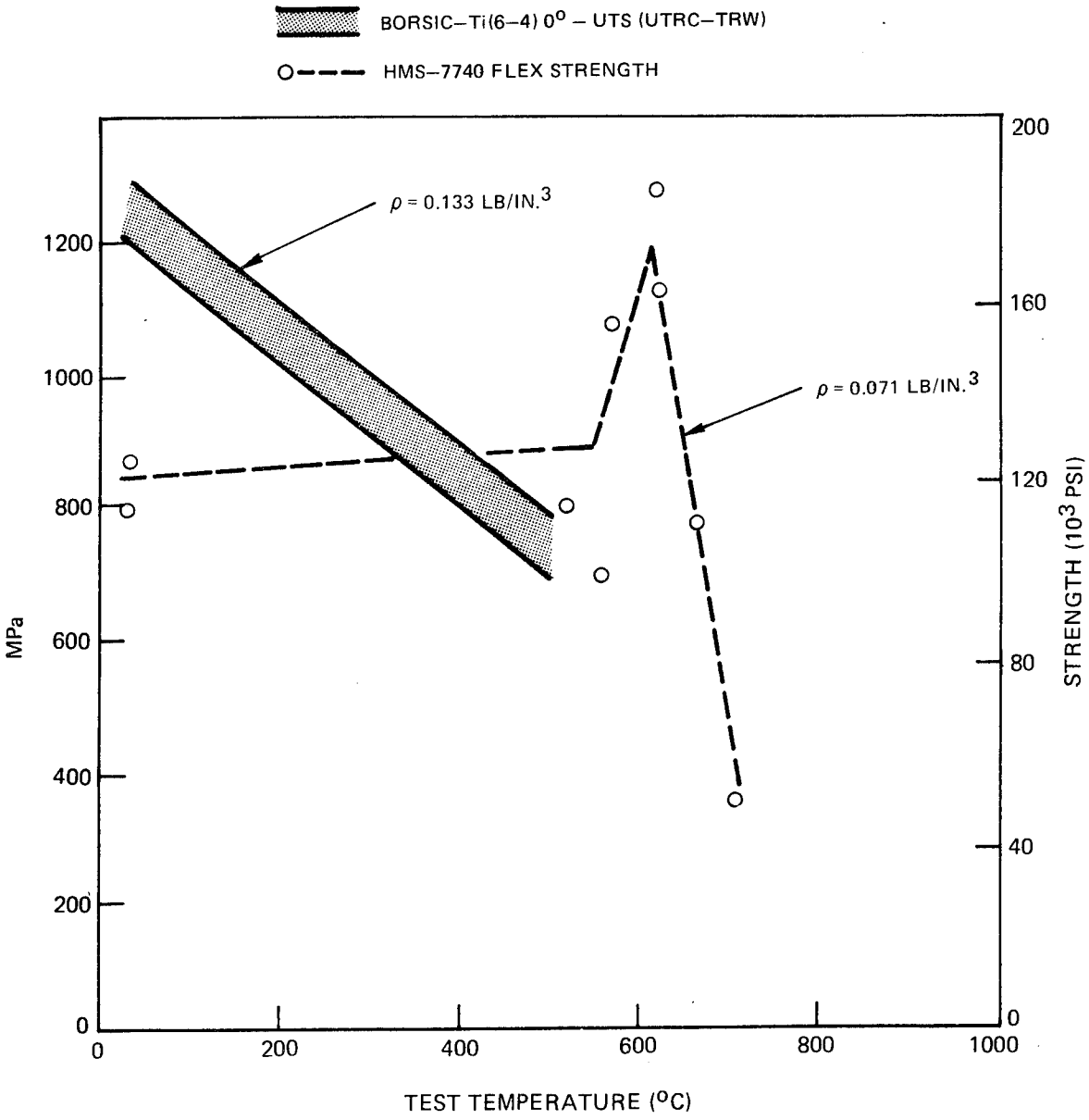
FIG. 36

SPECIFIC FLEXURAL STRENGTH COMPARISON



76–11–107–7

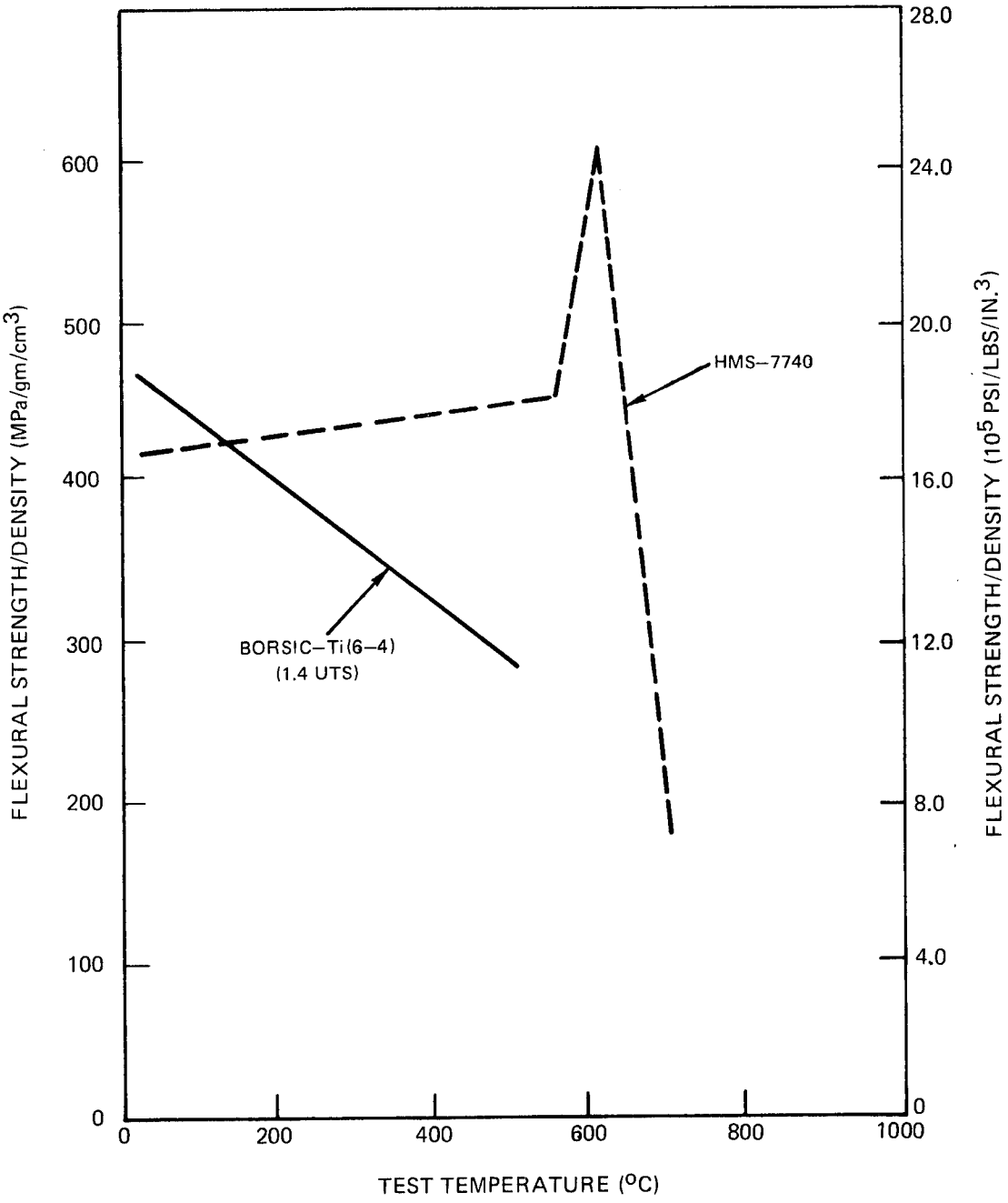
FLEXURAL STRENGTH COMPARISON



76–11–107–8

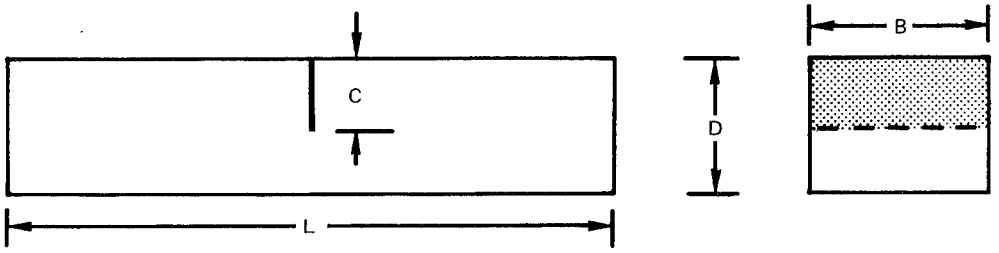
FIG. 38

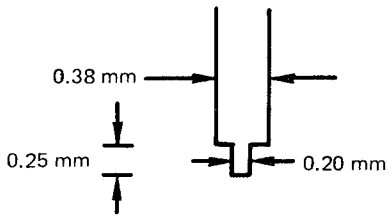
SPECIFIC FLEXURAL STRENGTH COMPARISON



76–11–107–9

FRACTURE TOUGHNESS SPECIMEN





NOTCH TIP CONFIGURATION

76–11–107–3

Table XXIII

Fracture Toughness Specimen Dimensions

Specimen	C (cm)	B (cm)	D (cm)	Test Span cm	L cm
LB-140-1	0.330	0.990	0.691	3.98	5.0
-2	0.305	0.990	0.691	3.80	5.0
LB-157-1	0.330	0.954	0.852	3.98	5.0
-2	0.330	0.954	0.852	3.98	5.0

Specimen Test Data

Specimen	Test Speed (cm/min)	Test Temp °C	K_c $MN/m^{3/2}$	K_c 10^3 psi $\sqrt{in}$	Energy Per Unit Area Joules/m^2	Energy Per Unit Area ft-lbs/in^2
LB-140-1	20,000	22	21.4	19.5	23,500	11.3
-2	0.127	22	22.1	20.1		-
LB-157-1	20,000	600	15.8	14.3	10,600	5.1
-2	20,000	650	19.0	17.3	11,800	5.7

The load vs deflection trace for the slow bend test is presented in Fig. 40. The increase in load to failure is linear and the value of fracture toughness of 22.1 $MN/m^{3/2}$ was calculated on the basis of the maximum load.

By comparison, the load-time traces for the instrumented impact tests are given in Figs. 41 and 42. The initial peaks in these tests are the inertial peaks which have to do with the high velocity of impact. Aside from these inertial peaks, the rise to maximum load is also nearly linear for these tests and the value of K_c was also calculated on the basis of the maximum load.

The data in Table XXIII indicate that at 22°C there was no effect of dramatically increasing test speed. The fracture toughness did, however, decrease with increasing test temperature. This is opposite to the variation in strength described previously; note that even the values obtained at the higher temperatures are greater when compared to other composites and more conventional engineering alloys, Table XXIV.

8. Effect of Thermal Cycling on Flexural Strength

Sample LB 135G, HMS in 7740, was tested by thermal cycling specimens at an interval of 8 minutes and 20 seconds as indicated by the thermal cycle shown in Fig. 43. As noted in Table XXV and as drawn in Fig. 44, the thermal cycling had little or no effect on the four-point bend strength of the specimens and these, after cycling, looked exactly as they had initially.

9. Fatigue Studies and the Effect on Flexural Strength

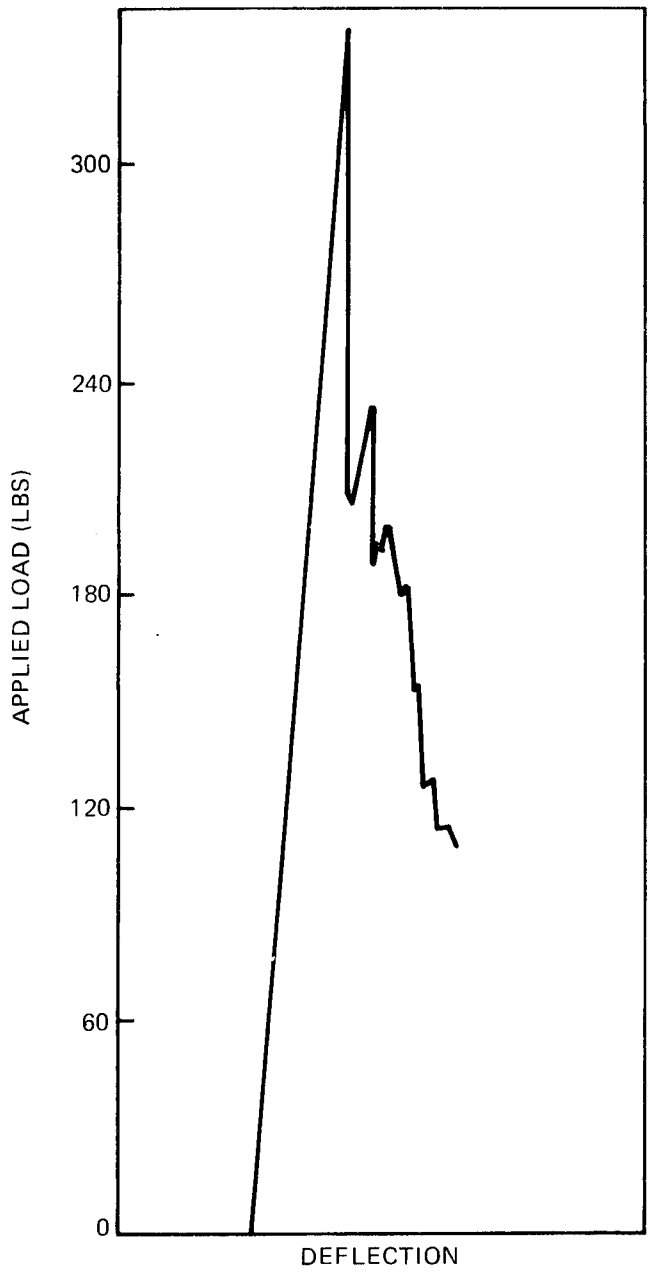
Sample LB 135, again an HMS graphite fiber in C.G.W. 7740 glass composite made in the Centorr press, was subjected to four-point flexural fatigue testing. These specimens were prefatigued to between 0.8 and 0.08 of the as-fabricated four-point bend strength. Table XXVI and Fig. 45 show that the samples suffered no deterioration in strength after 100 cycles.

10. Analysis of Graphite Fiber Content of HMS Composites

It has proven very easy to separate the graphite fibers from glass matrix using HF solutions. The fibers are recovered in a virtually intact condition and show no effect of having been encased in glass by hot pressing. In Table XXVII are shown the results of the analysis for two of the composites used in the tests of this section. The sample LB 138 has a three-point flexural strength of 661 MPa and 96,000 psi and was prepared in the older press used in this program as was sample LB 139.

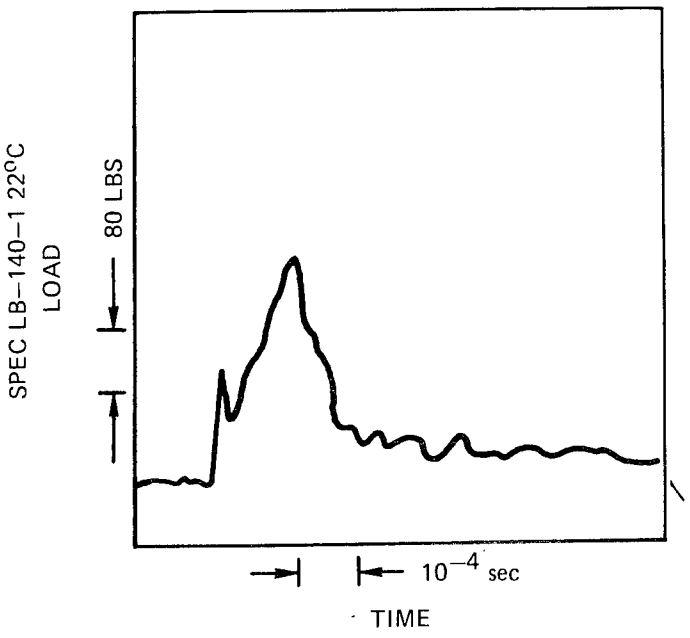
FIG. 40

LOAD VS DEFLECTION TRACE FOR SPECIMEN LB–140–2 TESTED AT 22°C



76–11–107–4

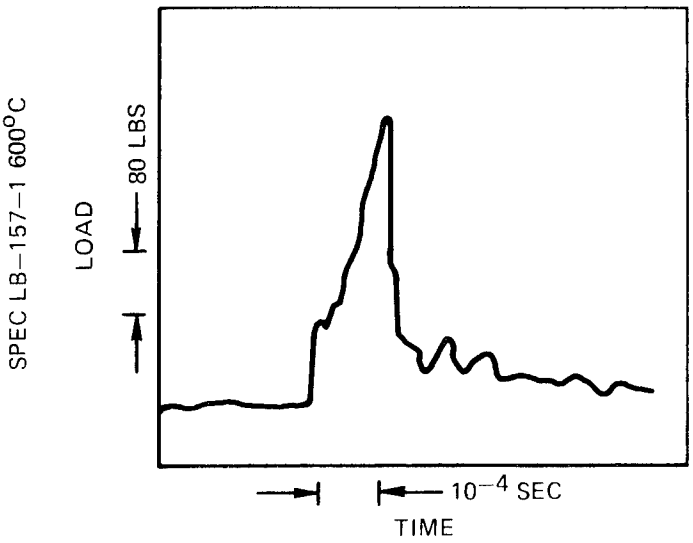
INSTRUMENTED IMPACT TRACE

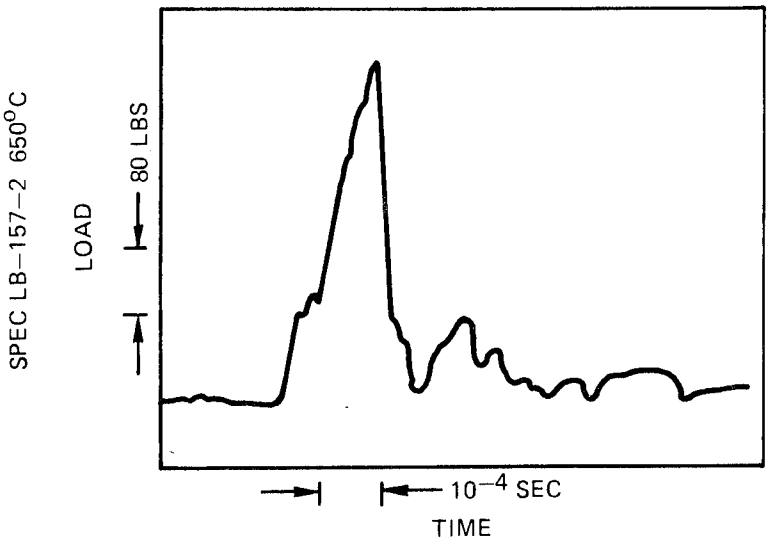


76–11–107–10

FIG. 42

INSTRUMENTED IMPACT TRACES





76–11–107–1

Table XXIV

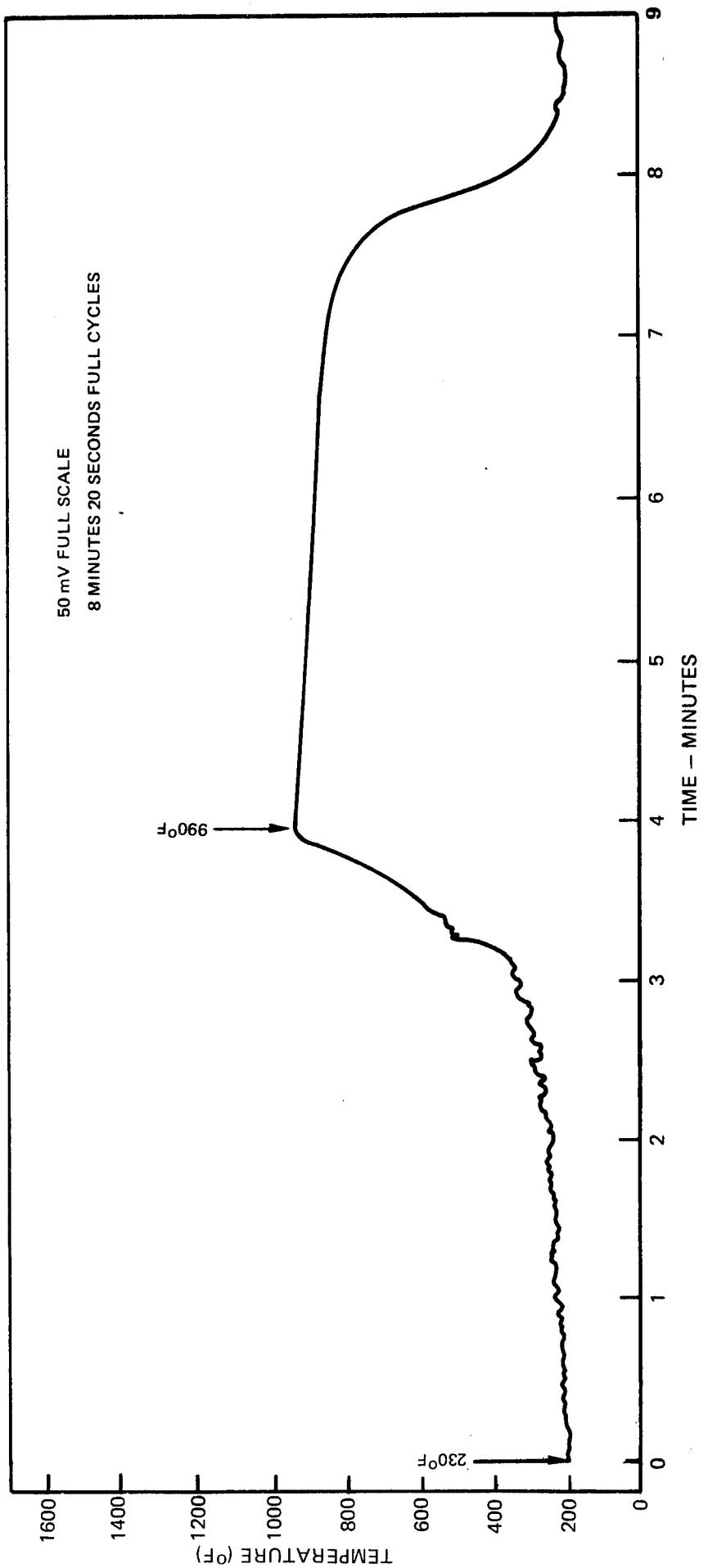
Fracture Toughness Comparison at 22°C

Material	K_{IC}	
	$MN/m^{3/2}$	10^3 psi $\sqrt{in}$
0°-HMS/7740	21.7	19.8
0/90-AS Graphite/AR 288*	14.25-1.973	13-18
Morganite II/Epoxy**		
0°	35	32
90°	1.75	1.6
45°	2.52	2.3
±45°	19.73	18
0/±45°/90	24.1	22
2014-T6 Aluminum Alloy***	21.92	20
6061-T651 Aluminum Alloy***	29.6	27

*UTRC data using compact tension specimens
**H. Konish and T. Cruse, J. Comp. Materials, Vol. 6, p 114, 1972
***Damage Tolerant Design Handbook MCIC-HB-01

FIG. 43

TEMPERATURE CYCLE



77-05-150-3

Table XXV

Thermal Cycling

HMS Reinforced 7740 Spec LB 135 G

Condition		4 Point Bend Strength MPa	4 Point Bend Strength 10^3 psi	*Elastic Modulus GPa	*Elastic Modulus 10^6 psi
As Fabricated		896	130	185	26.8
		938	136	196	28.5
		800	116	201	29.2
	Average	876	127		
After 20 Cycles **		917	133	196	28.5
		910	132	203	29.4
		834	121	189	27.4
	Average	889	129		
After 100 Cycles **+		786	114	174	25.2
		614	89	167	24.2
		758	110	185	26.9
	Average	717	104		

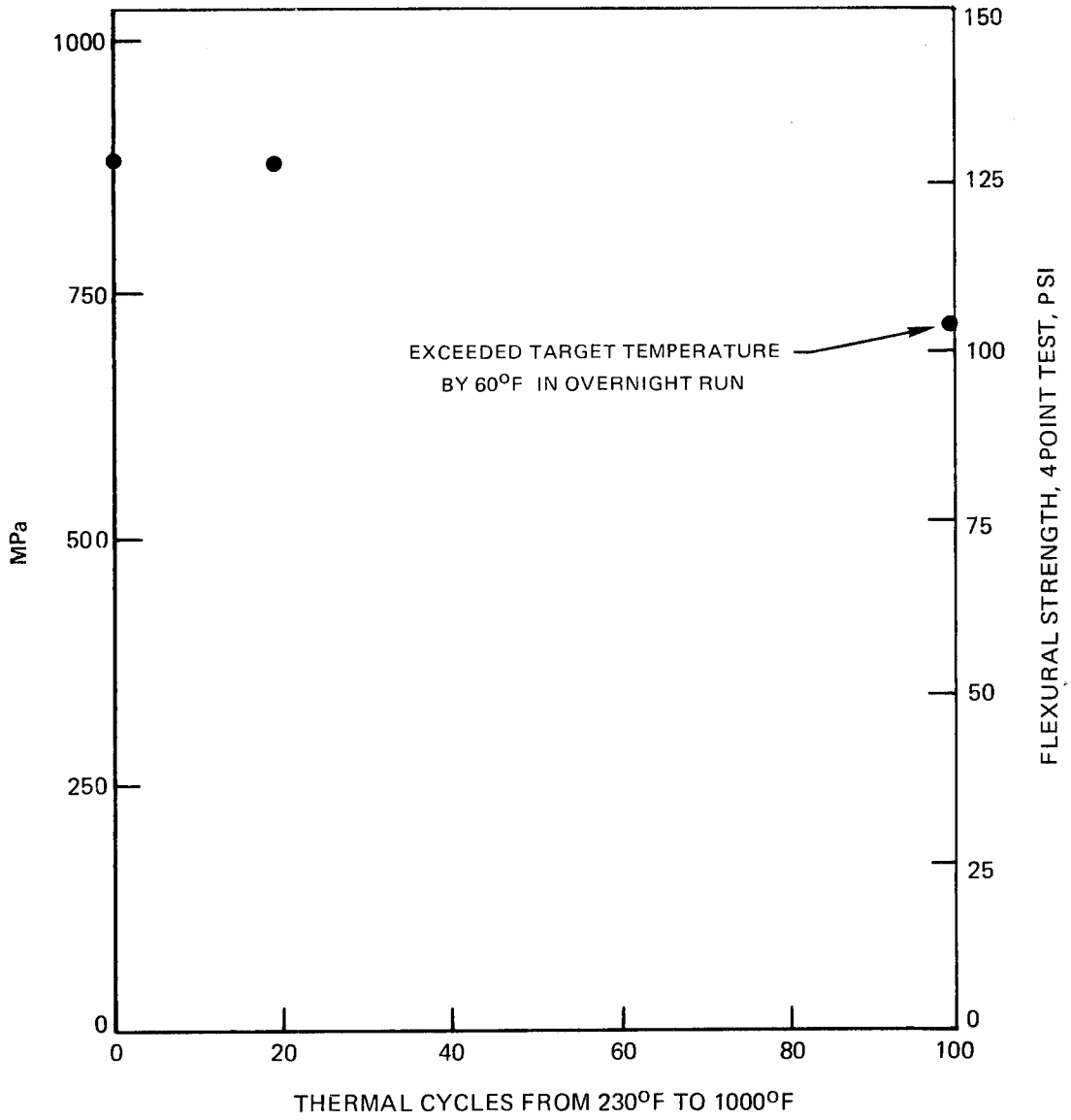
* Tested with major and minor spans of 5cm and 1.27cm

** Cycled while in argon containing glass tube between 590-630°C and 110°C Target temperature 560°C or annealing point of glass matrix

**+ The 100 cycles extended overnight with result that temperature exceeded target temperature (annealing point of glass matrix is 560°C or 1040°F) by 33°C.

FIG. 44

FLEXURAL STRENGTH OF HMS THORNEL 300–7740 GLASS COMPOSITE AFTER THERMAL CYCLING



77–05–150–4

Table XXVI

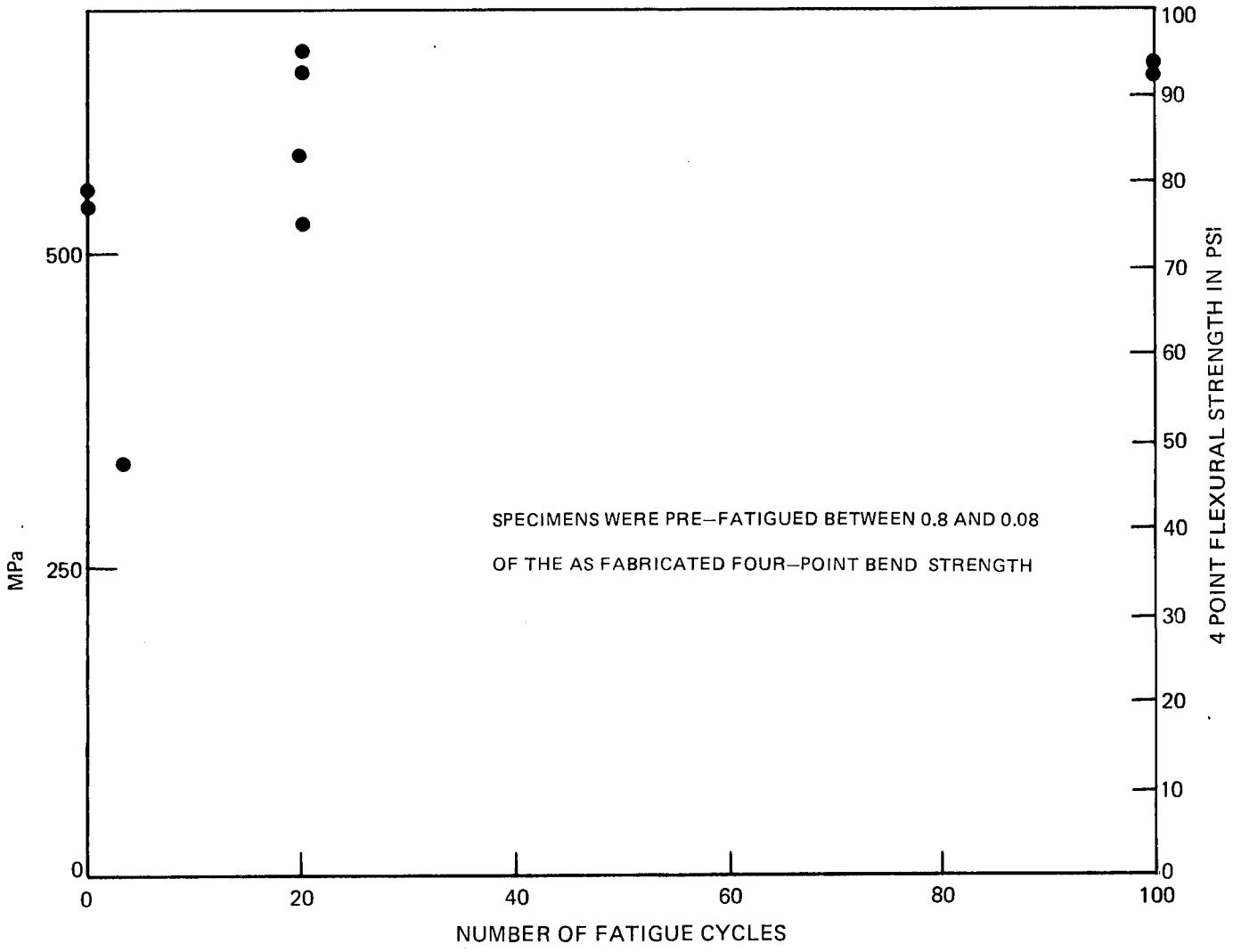
Four Point Flexural Fatigue
(Major and minor spans of 5 cm and 1.27 cm)

HMS Reinforced 7740 Spec LB 135 H

Condition	4 Point Bend Strength		Elastic Modulus	
	MPa	10^3 psi	GPa	10^6 psi
As Fabricated	548	79	200	29.0
	532	77	195	28.3
After 3 cycles between 484 GPa and 48 GPa	325	47	185	26.8
After 20 cycles between 337 GPa and 34 GPa	519	75	186	26.9
After 20 cycles between 390 GPa and 39 GPa	658	95	194	28.1
After 20 cycles between 450 GPa and 45 GPa	574	83	210	30.5
After 20 cycles between 520 GPa and 52 GPa	638	92	208	30.1
After 100 cycles between 430 GPa and 43 GPa	575	84	207	30.0
After 100 cycles between 445 GPa and 44 GPa	573	83	201	29.1

FIG. 45

EFFECT OF FATIGUE ON BEND STRENGTH OF HMS THORNEL 300 FIBER IN 7740 GLASS MATRIX COMPOSITE



77–05–150–5

Table XXVII

Determination of Graphite Fiber Content for Several
Graphite Fiber-Pyrex Glass Matrix Samples

Sample Identity	Vol % C	Vol % Glass	% Porosity	Weight % C	Weight % Glass	Analysis No.
LB 138 HMS	59.2	40.6	0.2	54.2	45.8	72340
LB 139 HMS	62.1	36.6	1.3	57.9	42.1	72341

B. Composites of Celanese DG-102 Graphite Fiber and Pyrex Glass

Because composites formed of Celanese DG-102 graphite fibers in Pyrex glass showed strengths only about one-third as great as the composites made with HMS graphite fiber in Pyrex glass, they have not been studied as extensively. But these same Celanese DG-102 graphite fibers in Pyrex glass composites have now been shown to have very much greater environmental stability than those made with HMS graphite fibers and Pyrex. Research during the second year of this program will attempt to produce composites with higher strength; we now obtain at room temperature only about one-third of the strength of the fiber in the composite that would be predicted based on the law of mixtures

1. Microstructure

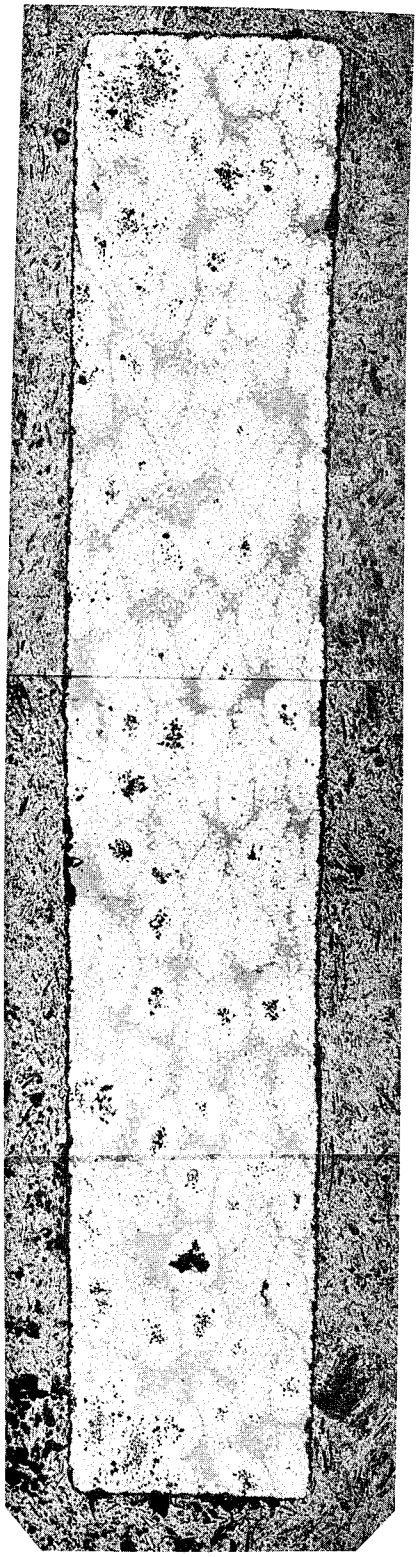
The typical microstructures found in the Celanese DG-102 graphite fiber-Pyrex glass composites are shown in Figs. 46 and 47. The optical tape map of Fig. 46 shows that in the composites of Celanese fiber made to date the memory of the individual tows persists. Figure 47 reflects the fact that a Celanese fiber-Pyrex glass tow fractures in a brittle-brittle manner just as one would expect with an all ceramic material and this is further emphasized by the scanning electron micrograph at the bottom of the figure, which shows again that each fiber is indeed surrounded by glass and very tightly bonded to it. It is this tight bonding that probably accounts for both the low strength of the composite and its superior environmental stability.

2. Effect of Atmosphere

The three-point flexural strength of several specimens of Celanese DG-102 graphite fiber reinforced Pyrex glass composites was measured at room temperature. Other specimens of the same composites were first heated for 4 hrs at 560°C in either air or argon before carrying out the flexural tests at room temperature. As Table XXVIII shows, within experimental error, the exposure to either air or argon had no effect on the properties of the composite in contrast to similar tests carried out on HMS graphite fiber reinforced Pyrex composites where the air exposure at temperature resulted in a very high loss of strength. While admittedly both of the composites tested for which the data are shown in Table XXVIII are well below the average strength of Hercules HMS graphite fiber reinforced Pyrex matrix composites the data of this table are important in nature since all other graphite reinforced glass composites tested by UTRC show a pronounced degradation in strength when heated in air and subsequently tested. Further research in this area is obviously necessary in an attempt to improve the strength of these composites while maintaining their unique environmental stability.

FIG. 46

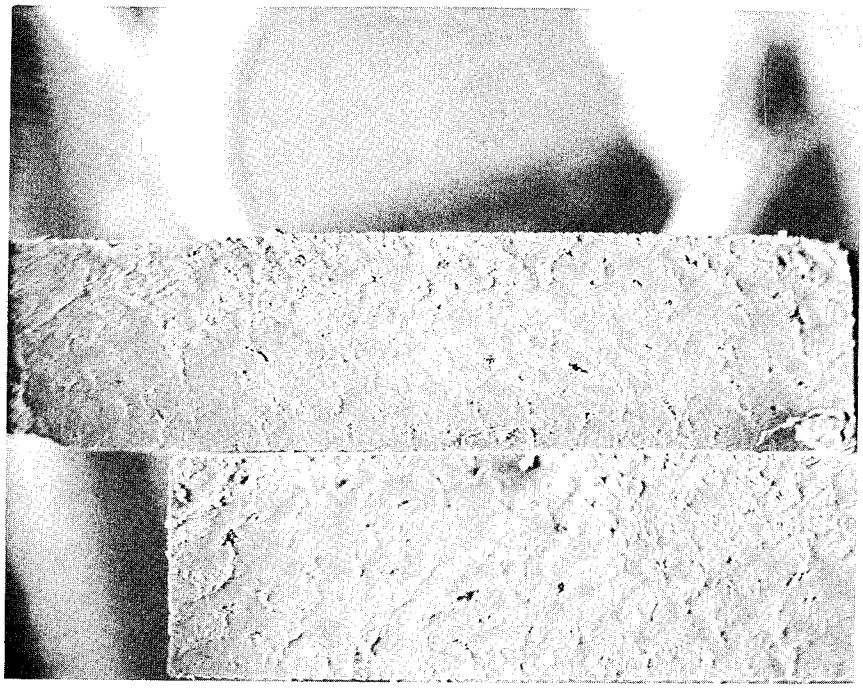
TAPE–MAP OF CELANESE DG 102 FIBER IN C.G.W. 7740 GLASS MATRIX–UNFRACTURED SAMPLE



76–06–292–8

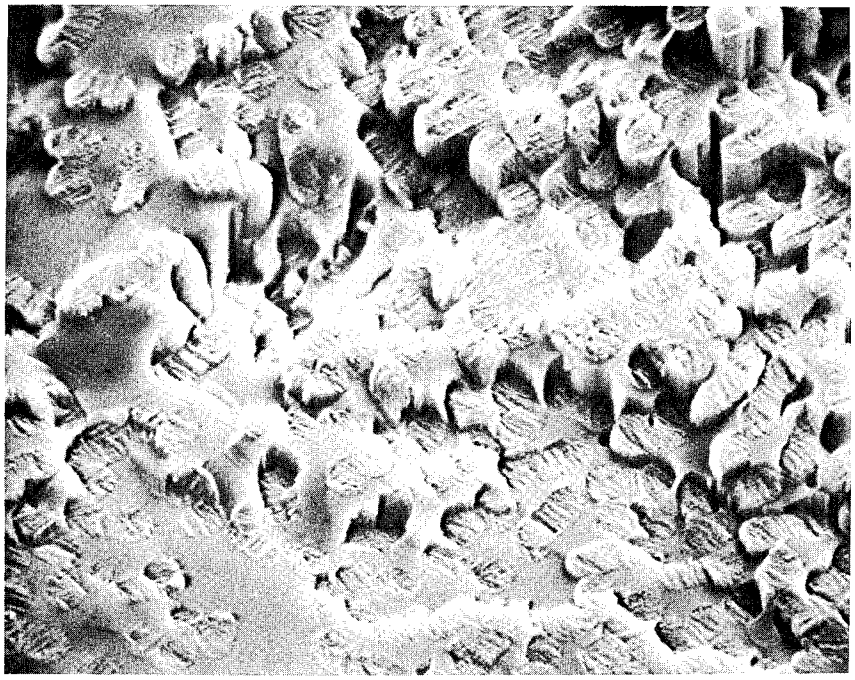
FIG. 47

SCANNING ELECTRON MICROGRAPHS FRACTURE SURFACE CELANESE DG 102 FIBER IN C.G.W. 7740 GLASS MATRIX



LB 91–R1

500μ



LB 91–L1

10μ

76–06–292–6

Table XXVIII

Effect of Atmosphere on Strength of Celanese DG-102 Graphite Fiber Reinforced C.G.W. 7740 Glass Composites

Specimen	Exposure Conditions			20°C 3-Point Bend Strength		
	Time	Temp.	Atmos.	MPa	10^3 psi	
LB-131	4 hrs	560°C	Argon	180	26.1	
				233	33.7	
				245	35.6	
				291	42.2	
				303	44.0	
				328	47.6	
				263	38.2	Avg.
LB-131		None		155	22.5	
				187	27.1	
				192	27.8	
				221	32.0	
				275	39.9	
				326	47.9	
				227	32.9	Avg.
LB-132	4 hrs	560°C	Air	145	21.1	
				188	27.2	
				202	29.3	
				234	33.9	
				280	40.6	
				308	44.7	
				226	32.8	Avg.
LB-132		None		172	25.0	
				225	32.6	
				228	33.1	
				241	34.9	
				279	40.5	
				312	45.3	
				243	35.2	Avg.

3. Typical Flexural Strength and Modulus

Table XXIX lists the three-point flexural strength, the four-point flexural strength, and modulus for two typical samples of Celanese DG-102 graphite fiber reinforced Pyrex glass composites. Sample LB 97 was hot pressed in an older press at 1100°C and 13.8 MPa (2000 psi) while sample LB 97E was produced in the new press at 1200°C and 13.8 MPa (2000 psi). While slightly stronger composites of this nature have been produced the values of this table are more typical and representative of this composite at this stage of development.

4. Flexural Strength at Elevated Temperatures

The Celanese fiber reinforced 7740 composite system was tested in three-point bend as a function of temperature. In carrying out these tests an argon atmosphere was used.

The test results for specimen set LB 98 are presented in Fig. 48 and Table XXX. As can be seen, there is a marked change in composite performance with increasing temperature. As the composite reaches the annealing point of the matrix glass, the composite flexural strength is nearly double the value at room temperature. This increase in strength is probably due to the increased strain capacity of the matrix. For this composite system, of Celanese fiber and 7740, the bond between fiber and matrix is very strong. Therefore, it is likely that the composite strength is limited by the matrix failure strain at room temperature. At temperatures above the strain point of the glass, however, the matrix can deform to a greater extent, because of its lower viscosity. Thus, a larger percentage of the fiber strain, and hence strength, can be utilized. At temperatures above the annealing point (560°C), a large decrease in strength is noticed, however, the strengths calculated above this temperature are fictitious because the specimens do not fracture; instead the specimens deform to a very large extent. This is illustrative of an even further drop in matrix viscosity. At 700°C the viscosity of 7740 is 10^{10} poises while at 510°C it is $10^{14.5}$ poises.

Examination of the specimen fracture modes confirms the above description. At room temperature the specimens fracture without any permanent deformation and very little fiber pull out on the fracture surface, Fig. 49. At 500-550°C there is also no sign of specimen plastic deformation, however, additional fiber pull out is visible on the fracture surface, Fig. 50. This fiber-matrix separation occurred on the tensile side of each specimen. Finally at 700°C, Fig. 51, the specimen does not fracture but instead deforms to the full extent of motion of the test apparatus. In the last figure of this series, Fig. 52, we show the manner in which the sample plastically deformed to fit the test plunger. At the time of deformation the sample was still carrying a load of 42,000 psi

Table XXIX

Flexural Strength of Typical Specimens of Celanese Graphite Fiber DG-102 Reinforced C.G.W. 7740 Glass Matrix Composites

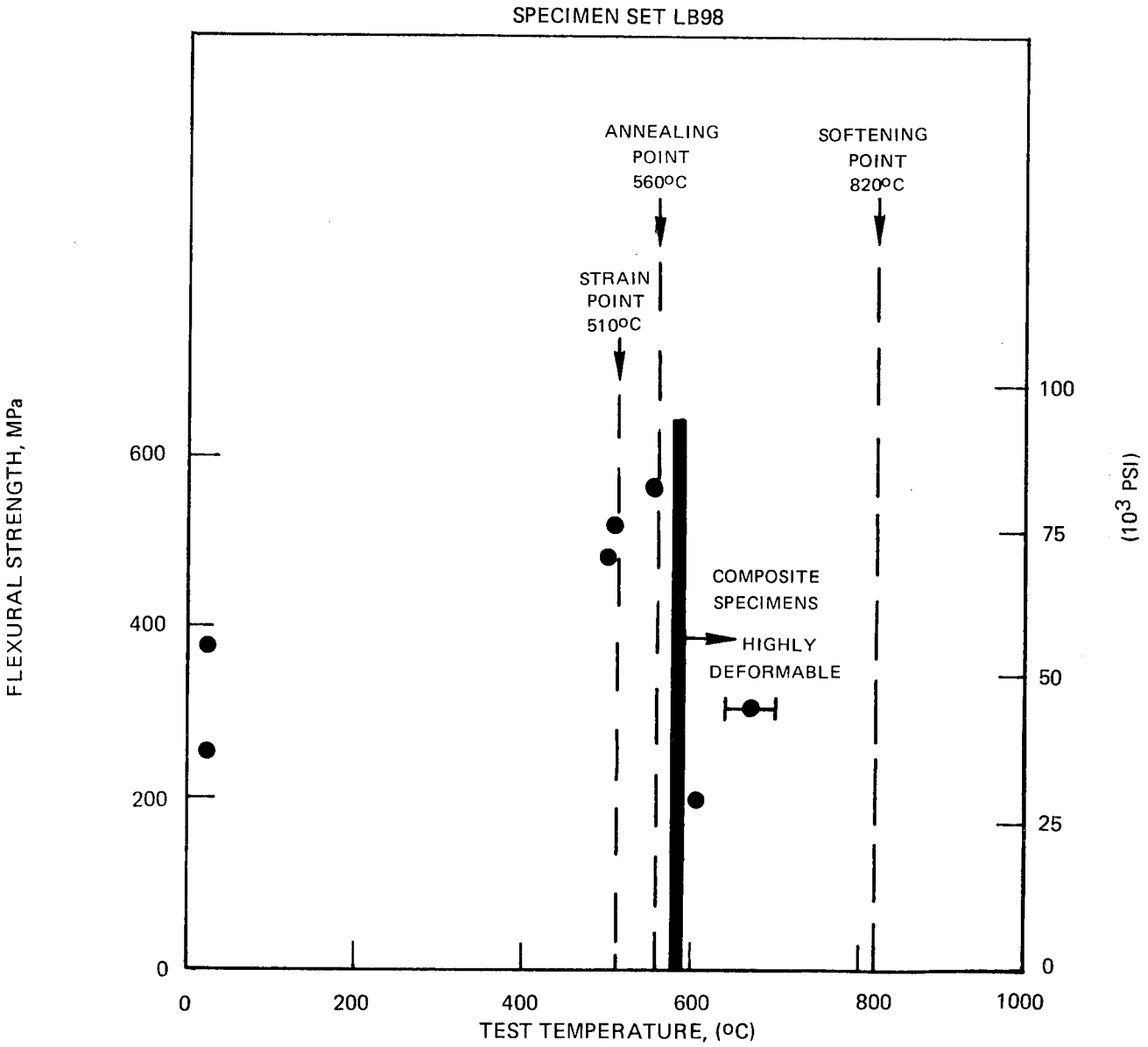
A. 3-Point Flexural Tests with 5.0 cm Span

Specimen LB 97	Flexural Strength MPa	ksi
L 1	399	57.8
L 2	411	59.6
L 3	265	38.4
C 1	339	49.1
C 2	340	49.3
C 3	293	42.5
R 1	281	40.8
R 2	362	52.5
R 3	392	56.8
Average	342	49.6

B. 4-Point Flexural Tests with Inner Span 1.25 cm and Outer Span 5.0 cm

Specimen LB 97E	Flexural Strength MPa	ksi	Modulus GPa	10^6 psi
TR	289	41.9	277	40.2
CR	301	43.7	269	39.0
BR	336	48.7	271	39.3
Average	309	44.8	272	39.5

FLEXURAL STRENGTH OF CELANESE FIBER REINFORCED 7740 GLASS AS A FUNCTION OF TEST TEMPERATURE



76–08–128–1

Table XXX

Flexural Strength of Celanese Graphite Fiber DG-102 Reinforced C.G.W. 7740 Glass Composite at Elevated Temperatures

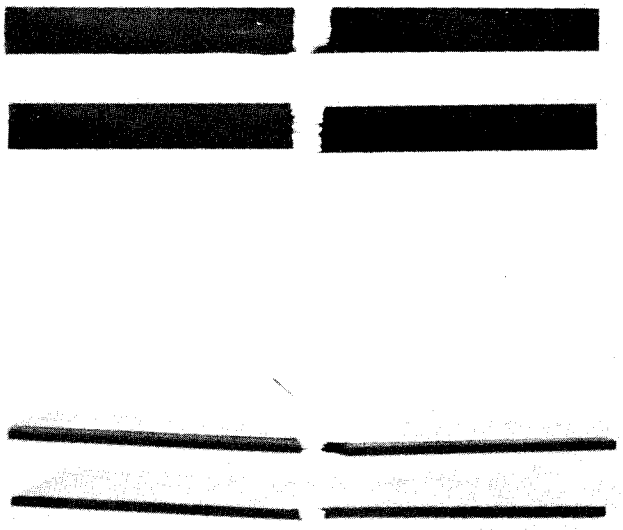
Specimen	Temperature at Which Flexural Strength was Measured °C	3-Point Flexural Strength Span 5.0 cm MPa	ksi
LB 98BL	RT	374	54.2
CR	RT	250	36.2
TL	500	515	74.7
BR	500	481	69.7
CL	550	565	82
TR	600	196	28.4
TC	700	292	42.3
CC	700-635	305	44.3

FIG. 49

CELANESE FIBER REINFORCED 7740

TEST TEMPERATURE 22 °C

LB–98



76–09–102–2

FIG. 50

CELANESE FIBER REINFORCED 7740
TEST TEMPERATURE 500–550 °C
LB–98

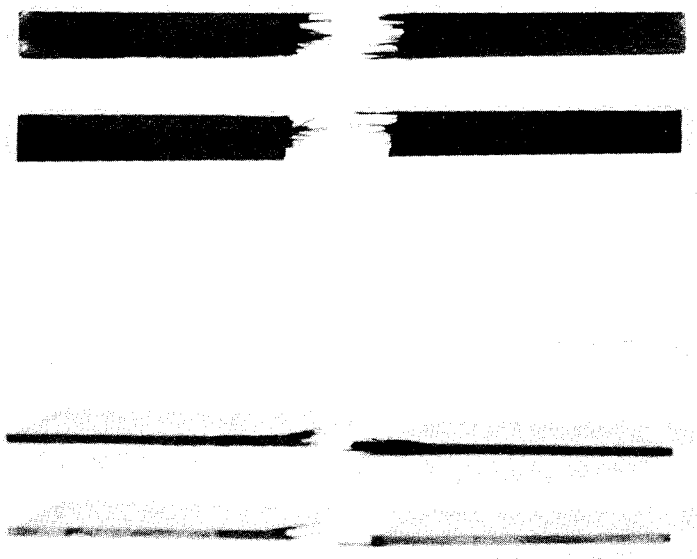
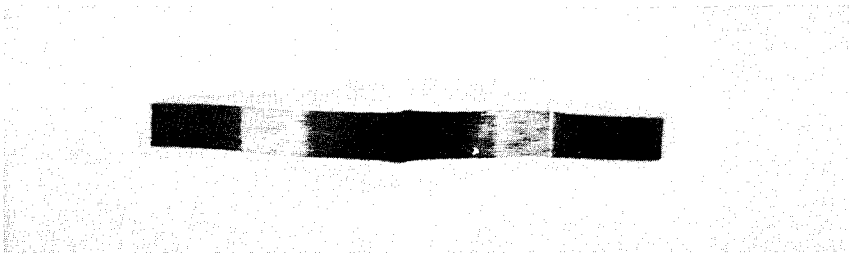


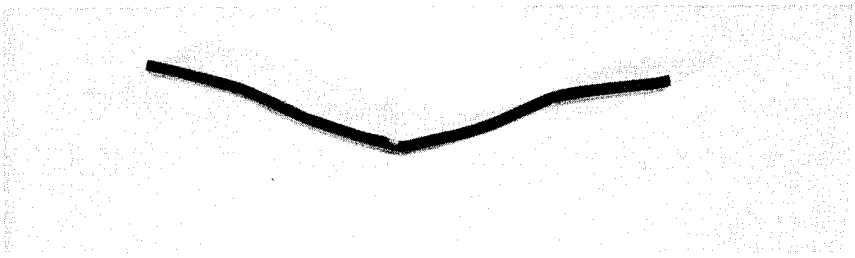
FIG. 51

CELANESE FIBER REINFORCED 7740

TEST TEMPERATURE 700 °C

LB–98



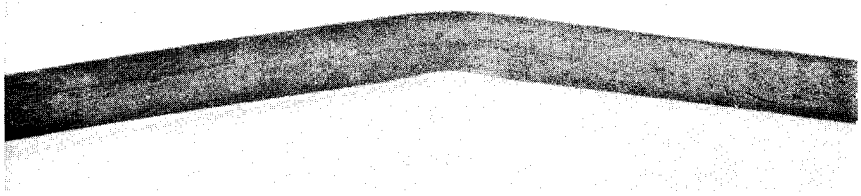


3 POINT BEND SPECIMEN LB98–CC

TEST TEMPERATURE = 700°C

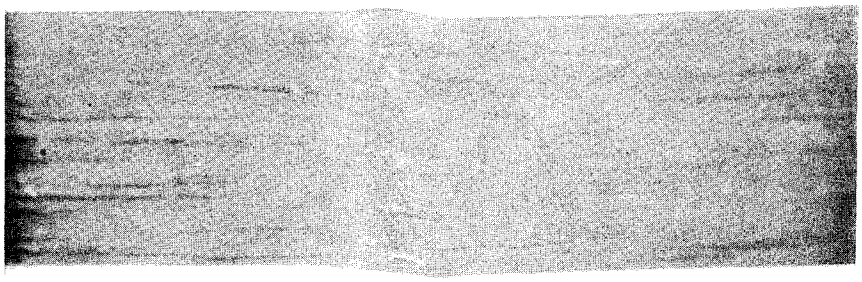
a) OVERALL SIDE VIEW

600 μ



b) AREA LOADING–SIDE VIEW

2000 μ



c) BUCKLED AREA OF CONTACT WITH LOADING NOSE –TOP VIEW

2000 μ

which is also the approximate room temperature flexural strength for these high modulus graphite fiber composites. This behavior may be compared to the deformation under load undergone by a graphite fiber epoxy resin matrix as it passes through the transition from brittle to ductile behavior.

From the above it would appear that a use temperature of up to 550°C would be reasonable for this composite system. Specimen performance approaches that of resin matrix composites tested at much lower temperatures. As an example, approximately 50% unidirectional Celanese fiber reinforced epoxy typically exhibits a tensile strength of 758 MPa (110,000 psi) at 22°C while the current composites of Celanese fiber reinforced C.G.W. 7740 glass fail at 345 MPa (50,000 psi) at 22°C and 565 MPa (82,000 psi) at 550°C for a volume percent fiber of 47%.

VI. CONCLUSIONS AND RECOMMENDATIONS

At the end of the first year's research, we have two principal types of graphite fiber reinforced glass matrix composites, each of which have some excellent but different properties.

The first type of composite consists of Hercules HMS graphite fiber reinforced C.G.W. 7740 glass matrix. Its properties are:

Room temperature 4-point flexural strength of 848 MPa (127,300 psi)
Average flexural modulus of 200 to 206 GPa (29 to 30 million psi)
Use temperature in argon or vacuum of 600°C (1112°F)
50% higher flexural strength at 560°C than at room temperature
No loss in strength with thermal or fatigue cycling in argon or vacuum
Greatly increased toughness compared to glass, i.e. about same as commonly used lower temperature composites
When heated in air to 560°C suffers severe loss of strength.

The second type of composite consists of Celanese DG-102 fiber reinforced C.G.W. 7740 glass matrix with these properties:

Room temperature 4-point flexural strength of 309 MPa (45,000 psi)
Average flexural modulus of 272 to 303 GPa (39.5 to 40 million psi)
Use temperature of 600°C again with 50% higher strength at this temperature than at room temperature
No loss in strength when heated in air to 560°C for 4 hrs and subsequently tested.

Based on the observations made during the first year's effort, the following recommendations are offered:

A systematic study of the mechanism controlling the oxidation of the HMS graphite fiber 7740 glass matrix composites at elevated temperatures should be carried out.

At the same time an effort should be made to partially block the bond between the Celanese DG-102 graphite fiber in 7740 glass matrices to see if a higher percentage of the strength of the graphite fiber can be attained while maintaining the oxidation resistance of these composites.

The number of graphite fiber, glass and/or Pyroceram matrix combinations should be expanded and evaluated to see if some new combination can offer both strength and oxidation resistance.

Biaxially reinforced specimens should be fabricated and evaluated.

An extensive characterization of the properties of the best graphite fiber-glass matrix system should be undertaken to provide a better understanding of how such composites can be used.

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